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DOTTORATO DI RICERCA IN SCIENZE DELLA TERRA
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GEOCHEMICAL AND ISOTOPIC STUDY OF SOILS AND WATERS FROM AN ITALIAN CONTAMINATED SITE: AGRO AVERSANO (CAMPANIA)

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“Try and leave this world a little better than you found it”

Sir Robert Baden-Powell

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1 Introduction

1.1 The S.I.N.s and the Italian Environmental Law 152/06

In 1998, the Italian Ministry of Environment (Ministero dell'Ambiente e della Tutela del Territorio e del Mare) defined, with the Law n. 426, a list of 15 S.I.N. (Siti di Interesse Nazionale – National Interest Sites), located throughout all Italy. In the following years, with the emission of further laws (388/00, 468/01, 179/02, 266/05 and 152/06), the number of these sites increased up to 54. In this category have been included all those highly polluted areas that, both for their extension and their historical and present land use, have been considered to be particularly at risk for human health. For these areas special attention and specific remediation activities are needed.

Many of these sites are areas once used for industrial activities with a high impact on the environment (petrochemical industries, asbestos fiber production), but also ex mining districts and big dumps. Four of the 54 Italian S.I.N. are in the Campania region and are:

- Napoli Orientale,
- Napoli Bagnoli-Coroglio,
- Vesuvian Littoral areas,
- Domitio-Flegreo Littoral and Agro Aversano area.

The latter site is one of the widest S.I.N. in Italy (1564 Km^2); it's located in north-western Campania and includes 77 municipalities belonging to both Naples and Caserta provinces (Fig.1).

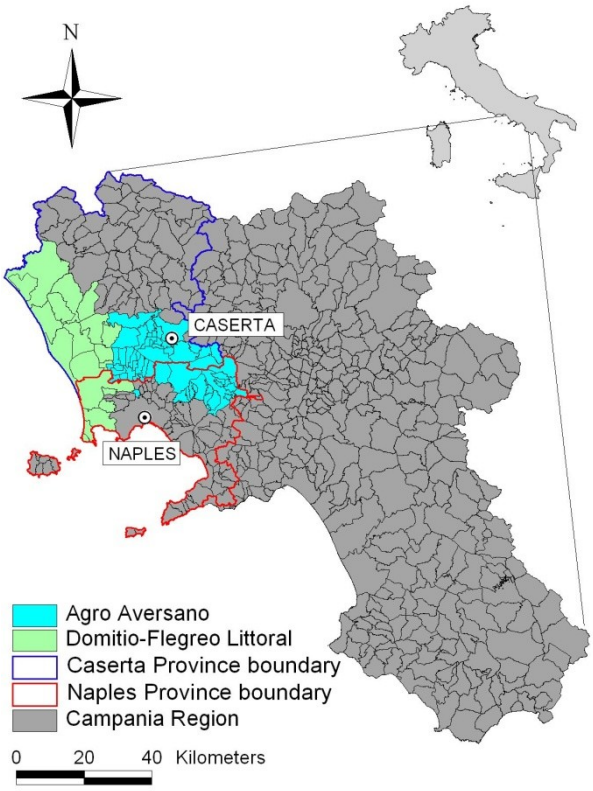


Fig.1 – *Geographical localization of the studied area*

Due to the wide extension of the whole S.I.N., the environmental study conducted on it, has been split in two, almost parallel, works, in order to better operate, especially during field activities and sample preparation phases.

In the present study, the attention has been focused on the Agro Aversano sector of the S.I.N. (about 700 Km^2); results of the study realized on the Domitio-Flegreo Littoral are reported in Grezzi et al. (2010, this issue).

1.2 Use of Pb isotopes in environmental studies

During the last 60-80 years, the rapid increase and development of human activities such as industrial plants and intensive farming, has brought about great changes into the environment, and has introduced new risks and hazards for nature and human beings. In order to characterize the affected environment, the use of tracers and environmental indicators, has been a widely diffused and effective operational tool.

Many studies conducted since the 70-80's in different countries and on different analyzed media, have all led to the opinion that Pb isotopes are some of the best tracers to be used for environmental purposes.

Lead is one of the most toxic and harmful element for plants, animals and humans. Its presence into the environment, can be related to both natural and anthropic origin, the first deriving from the Pb-rich rock weathering, and the last mainly deriving from the combustion of gasoline and from industrial smelting. These anthropic activities introduce into the environment very large amounts of Pb; according to some scientific works (Shirahata et al., 1980; Flegal et al., 1989; Nriagu, 1989) its anthropogenic pollution is estimated to account for 96-99% of the total atmospheric Pb deposition. Air is the chief way through which anthropogenic Pb is released and widespread; activities such as smelting, waste incineration, car exhausts and mining, introduce it in the atmosphere as airborne and particulate. Through air circulation, Pb can be transported even for long distances and, then, be deposited on soils. Once in soils, it can be absorbed by plants and enter in the food chain through the ingestion of contaminated plants by animals, thus influencing the entire biological cycle. In soils, Pb mainly concentrates in the surface horizon; nevertheless in some cases (Sterckeman et al., 2000; Denaix et al., 2001; Citeau et al., 2003; Jensen et al., 1999) its downward migration may occur and anthropogenic Pb can reach the groundwaters. This phenomenon can increase Pb contents also in the aquifers and seriously compromise the health of the environment and of the whole ecosystem, even on a large scale.

In Western Countries the major peaks of Pb concentrations in air have been registered during the 70's and the 80's, when lead alkyls were widely diffused as antiknock agent in petrol (Flament et al., 1996; Von Storch et al., 2002). Due to the well-known Pb toxicity, the use of these alkyls in the gasoline production, has been gradually banned by some Country Authorities, even if, in most of the developing countries it's still widely used. The introduction of unleaded gasoline in Europe and in countries such as Canada, USA and Japan, has slowly changed the isotopic composition of atmospheric aerosols, and the industrial processes have become the main sources of Pb contamination (Rosman et al., 1994; Veron et al., 1999a,b).

The reason why Pb isotopes are so commonly used as tracers of anthropogenic pollution, is their very high isotopic stability even after very long periods.

The isotopic fingerprint of a Pb source is the result of the age of the ore body itself and its initial U, Th and Pb contents (Doe, 1970). This means that, the isotopic ratios measured, for example, on an industrial waste, reflect the same isotopic ratios of the source in which has been extracted the Pb used for that specific industrial process. Lead isotopes, can, therefore, be considered to be a reliable source tracer, but also an useful tool to follow the migration and the distribution patterns of the elements through the different media.

In Campania Region Pb isotopic studies for environmental purposes have started in recent years: in 2002, Pb isotopes have been used to characterize an industrial site under remediation in the Neapolitan area (Bagnoli) (Tarzia et al., 2002), in 2008 Cicchella carried out a research on the Pb contents in the urban soils of Naples (Cicchella et al., 2008) and in 2009 isotopic studies on soils and groundwaters of the Domitio-Flegreo Littoral have been realized by Grezzi (Grezzi et al., 2010). In these three works the obtained results strongly suggest a mixing between two main end-members: one of natural origin (geogenic) (Ayuso et al., 1998; Gilg et al., 2001; Somma et al., 2001; D'Antonio et al., 1995) and one deriving from anthropic sources.

1.3 Aims and phases of the research

Unlike most of the other S.I.N.s, whose contamination is the result of a clear and specific kind of human activity, such as petrochemicals or foundries, in the Agro Aversano the contamination is the result of a bad administration of the territory and of an unknown number of environmental crimes acted for decades by the criminal organization known as "Camorra".

The object of this environmental study is to characterize, geochemically and isotopically, a land on which no previous scientific work were realized, in order to better understand: the degree of the contamination, the sources that have caused it, and improve the knowledge about the pathways for contaminants diffusion throughout the environment.

The whole study developed in two main and well distinct phases:

- the first has been a preparatory phase in which, through different media sampling and related data elaboration, has been possible to select the areas where concentrate the Pb isotopic studies;
- the second part of the research is the one focused on the Pb isotopes analysis and on the interpretation of the obtained data.

In the first part of the study, a homogeneous sampling of 113 surface soils (5-20 cm), 20 samples from 2 soil profiles (0-1 m), 11 stream waters and 4 groundwaters, was carried out. The whole field activity was realized on the basis of a sampling grid made up of 166 square cells of 5Km^2 extension each; FOREGS sampling procedures (Plant et al., 1996; Salminen et al., 1998) have been strictly followed during all the steps.

After their preparation in the Laboratories of the University of Naples, surface soils samples have been analyzed to determine the concentrations of 50 elements, by using the ICP-MS technique. Obtained data have, then, been statistically and cartographically processed,

thus giving the possibility to do the first and basic remarks on the major elements distribution in soils and on the contamination level of the investigated area. First considerations have been made also taking into account the limits fixed by the 152/06 Italian Environmental Law. The production of the basic geochemical maps and the related statistical studies, have been a propaedeutical and very useful tool to better address the second and most important step of the study.

The second phase of the research has been carried out in the Radiogenic Isotope Labs of the United States Geological Survey (USGS) located in Reston, Virginia. Here, 20 selected surface soils, 20 samples collected along two soil profiles at different depth, 11 stream waters and 4 groundwaters have been passed through a long and scrupulous chemical preparation (Ayuso et al., 2003), and, then, analyzed with the Thermal Ionic Mass Spectrometer (TIMS) in order to obtain their Pb isotopic ratios.

To better trace which could more likely be the contamination sources for soils and waters, three samples of the most commonly used pesticides in the area (Azin Pb30, Cosan's and Crittam WG) have been processed through TIMS (Grezzi et al., 2009) and then used as one of the anthropic end-member in the interpretation of the data.

Through the cross-study of isotopic data, local geological and mineralogical characteristics and their spatial variability, properties of the sampled media and the kind of urban settlement developed, it has been possible to have a more clear picture about how do the human activities influence the nature, and how do the soils and the waters react to the pollution.

2 The Agro Aversano

2.1 Studied area

The Agro Aversano is an area extended about 700 Km^2 located in northern Campania. It's made up of 57 municipalities, belonging to both Neapolitan and Caserta provinces and including Caserta town. A so large number of urban settlements on such an extended area (Domitio-Flegreo Littoral includes 26 municipalities in about 864 Km^2), is the reason for the very high urbanization rate found on it.

Notwithstanding this, there are some substantial differences between the municipalities belonging to Naples (south-eastern sector) and those belonging to Caserta (northern and north-eastern sector). Towns in the south and in the east of the area, are the Neapolitan suburbs; they are highly urbanized and create an intricate mosaic of small and very small municipalities where no interruptions between each other can be recognized. On the other hand, towns of the Caserta province have usually bigger extensions and, although the presence of very big towns (Maddaloni, San Tammaro, Capua, Marcianise, etc.), especially to the west, there are large areas addressed to agricultural activities.

The main municipalities of the Agro Aversano are: Caserta (with a population of about 79.000 in 54 Km^2), Acerra (with a population of about 55.000 in 54 Km^2), Aversa (with a population of about 52.000 in 9 Km^2), Marcianise (with a population of about 40.100 in 31 Km^2), Pomigliano d'Arco (with a population of about 39.000 in 11 Km^2) and Maddaloni (with a population of about 38.700 in 36 Km^2).

2.2 The Campanian Plain

The Agro Aversano is located in the middle part of the Campanian Plain (Fig.2), a big graben, probably originated in the Lower Pleistocene, which, during all the Quaternary, developed with a subsidence velocity of about 1.5-2 mm/year. Alluvial deposits deriving from the Apennine erosion, and volcanites deriving from both ancient volcanic complexes, now buried, (Parete volcano and Pre-Somma volcano) (De Vivo et al., 2001; Rolandi et al., 2003) and from the modern complexes of the Campi Flegrei and Somma-Vesuvio, have gradually filled the subsident graben. The Campanian Plain is delimited by NE-SW and NW-SE normal faults that lowered part of the Apennine Carbonatic Platform which now represents the substratum of the whole Plain (De Vivo et al., 2006a).

According to Scandone (1979), the Campanian Plain was generated by the same tectonic processes that caused the opening of the Tyrrhenian Sea and the counterclockwise rotation of the Italian peninsula.

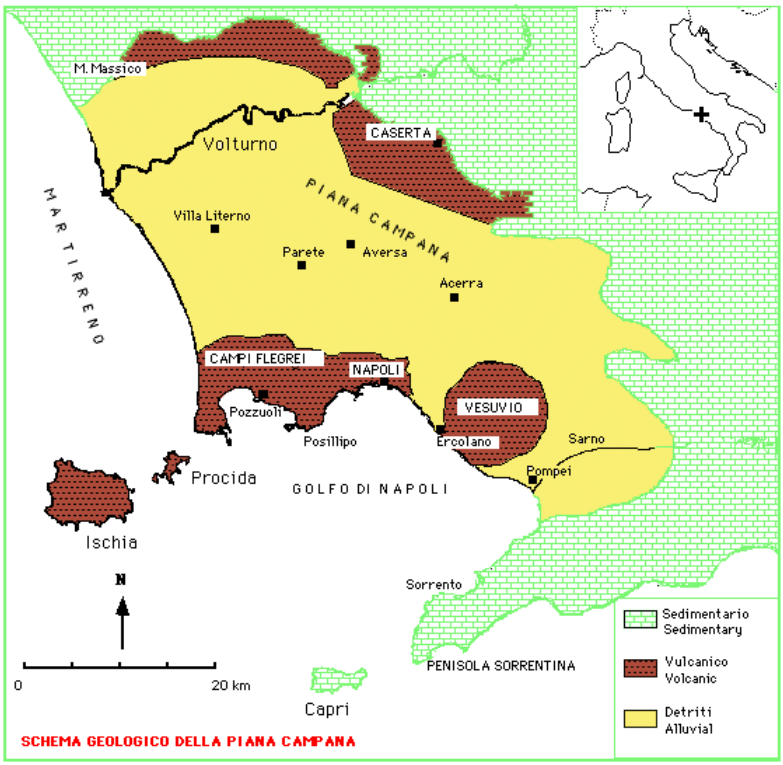


Fig.2 – *Sketch of the Campanian Plain*

2.3 Geomorphology and hydrography

The studied area, lying in the Campanian Plain, is mostly characterized by flat morphologies, from the northern boundaries of Caserta town to the Neapolitan suburbs. Morphology becomes hilly in the eastern sector of the investigated area, near the municipalities of Visciano, San Felice a Cancello, Maddaloni and Santa Maria a Vico, where the presence of the near Apennine starts to be more evident. The area can be seen as an alluvial plain delimited by the carbonatic complexes of the Aurunci Mts. in the NW sector, by the Caserta Mts. in the north, by the Avella Mt. in the NE part and by the Lattari Mts. in the south.

The upper border of the Agro Aversano is represented by the natural hydrographic limit of the Volturno river, whose average flow of about 82m^3/s, is the highest of all southern Italy. It rises in Capo Volturno, in Molise region, and has a length of about 175 Km; in its transit in the Campanian Plain it flows as a meander channel and then finally reaches the sea near Castelvolturno town, in the Domitio-Flegreo Littoral.

The main hydrological feature that characterizes the Agro Aversano is the Regi Lagni artificial channel. It is the product of a drainage and canalization work of the ancient Clanius river, acted by the Bourbons in the 1610. Since then, the areas surrounding the river, have no longer been plagued by the floodings that previously affected the territory and population living nearby. The realization of such a big environmental work has a great historical importance since it gave development chances to the area that, until then was totally useless for every kind of purpose.

The Regi Lagni consists of different straight channels (Fig.3) that collect the meteoric and the spring waters and carry them from the plain to the north of Naples, toward Nola and

Acerra and, then, to the sea, for a length of about 56 Km. Its mouth is located between the Volturno's mouth and the Patria Lake.

Fig.3 – *One of the artificial channels of the Regi Lagni river (Località Astragata*)

Nowadays the Regi Lagni channel is in a completely careless condition, in total contrast not only with its historical importance, but especially, with its environmental role in terms of the improvement of the territory conservation.

2.4 Geology

The geology of the Agro Aversano can be easily summarized into three main lithologic units (Fig.4):

- carbonates,
- volcanites,
- alluvial deposits.

The carbonatic lithologies outcrop in the north-eastern part of the area, from the north of Caserta to Visciano. They are mainly limestones and dolomites of the Apennine Carbonatic Platforms. The basement of the whole Campanian Plain is made of the same kind of lithology.

After the subsidence of the carbonatic units, the graben was filled by lavas, tuff, lapillus and other volcanic products originated by the different eruptive phases of the many volcanic complexes that occur on the area, from the ancient buried volcanoes as the Parete and the Pre-Somma, to the Campi Flegrei (De Vivo et al., 2001; Rolandi et al., 2003) complex. In the northern sector of the Agro Aversano the volcanic deposits turn into Campanian Grey Tuff, also known as Campanian Ignimbrite (De Vivo et al., 2001; Rolandi et al., 2003).

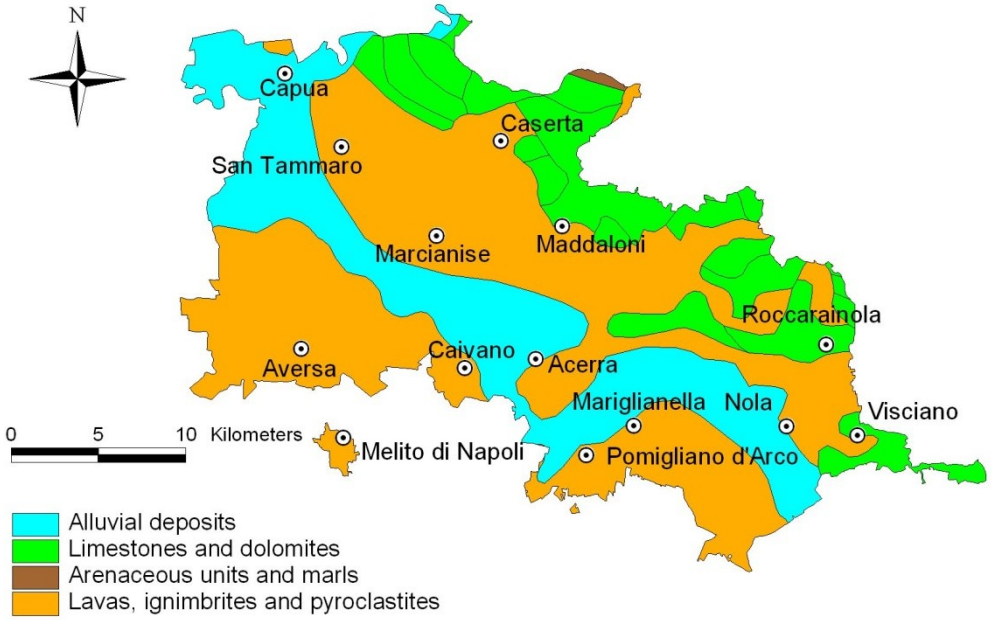


Fig.4 – *Lithological map of the Agro Aversano*

The alluvial deposits that fill the graben are mostly silty and clayey-sandy sediments transported and deposited by the Volturno river. The thickness of the sedimentary deposits of both alluvial and volcanic origin, varies in the space across all the Plain, but usually is over 100 m thick.

2.5 Land use

In an environmental study, one of the key factor to get good results, is the knowledge of the kind and the number of the activities that could alter the ecologic and biologic balance.

Looking at the land use map of the Agro Aversano (Fig.5) is possible to get a first idea of the economic activities distribution on it. Wide areas, especially to the west, are addressed to cultivated fields (mostly olives, vineyards, fruit trees and tomatoes); across all the Agro Aversano are also distributed a large number of highly urbanized centers (mainly concentrated in the Neapolitan suburbs, around Aversa and to the south of Caserta town) and relative industrial activities.

The main sources of pollution that can affect our investigated area are: farming and agriculture, urban and industrial settlements and road traffic.

Agricultural practices are, without any doubt, one of the most important economic activity of the Aversano area. Since past times, the presence of the volcanic soil, which is fertile by nature, has helped the development of many agricultural activities. Nowadays many of the farms found in this area have still a “familiar dimension”, but many others have expanded and become more similar to small industries. In the Agro Aversano, farms and dairies specialized in the “mozzarella” cheese production, have a great relevance. Obviously, the presence of a large number of dairies involve the presence of many bovine and cow buffaloes breedings. The main environmental problems associated to intensive agricultural

practices are those related to the large use of pesticides and fertilizers, and their migration processes through irrigation waters. In order to better understand how do these factors influence the environment, some of the pesticides more used in the area (Azin PB30, Cosan's and Crittam WG) have been analyzed with a Thermo Ionic Mass Spectrometer (TIMS) and studied to obtain informations about their distribution patterns in the different environmental media.

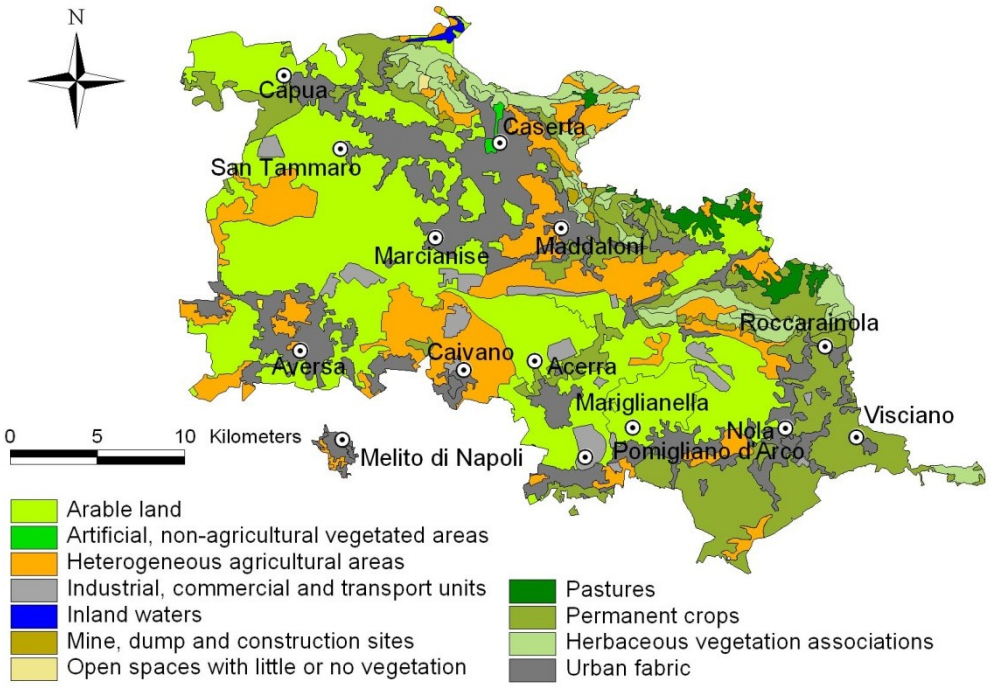


Fig.5 – *Land use map of the Agro Aversano*

Industrial activities and road traffic are the others main factors that contribute to the pollution of the Agro Aversano. In the Phlegrean area, over the southern border of the Agro Aversano, industrial plants like those of the ILVA, Eternit, Cementir and Federconsorzi (De Vivo, 2007) have been great social and economic development factors of the area for many years, but, at the same time, have strongly altered the surrounding environment in terms of soils, seawaters and air pollution. Most of the Pb once used in the Bagnoli industrial area, was mainly coming from the Broken Hill mine in Australia but also from Peru, Mexico and Italy (De Vivo, 2007).

The high density of the vehicular traffic throughout all the area greatly influences the concentrations of toxic elements in the air first and, in soils and waters later. In Italy the main company in the production of gasoline additives is the *Società Italiana Additivi Carburanti* (SIAC), the Italian affiliate of the *British Associated Octel* (AOC) company.

Although this general framework of the potentially pollutants activities of the Agro Aversano seems to be quite clear, the biggest environmental risk for this area is not related only to them. The main reason for the Agro Aversano inclusion in the S.I.N. list, is the presence of tons of special wastes, often really dangerous, illegally released in the soils, by the organized crime, for more than 25 years (Rapporto Ecomafia, Legambiente). The disposals of particularly harmful wastes, occurred in unauthorized dumping, in not

hydrogeologically isolated quarries, in agricultural soils, along the river banks and so on. In the recent years a new alternative "dumping technique" has widespread: the illegal incineration of the dangerous wastes in open air. The effect of this practice on the atmosphere is the production of an incredibly large amount of dioxins and furans, and the related direct contamination of air, soils, aquifers, plants, fruits, vegetables and pastures, and, therefore, the rapid poisoning of cattle and humans.

The consequences of a such highly uncontrolled and harmful contamination, will tragically affect this land and its inhabitants for next generations to come.

3 Sampling

3.1 Introduction

In order to have a good and spatially well extended knowledge about the major elements concentration in the Agro Aversano, different kind of environmental media have been sampled: surface soils, soil profiles, stream waters and groundwaters.

All the sampling procedures have been done on the basis of a square grid made of 166 cells of 5 Km^2 extension, overlapped to the whole studied area (Fig. 6); every cell has been uniquely identified by an alphanumerical code (i.e. AV001).

Every sampling phase and every sampling site has been documented by pictures and notes taken during field activities; all these data have been put together into an appropriate database in order to make easier the localization of each site for further investigations or comparisons.

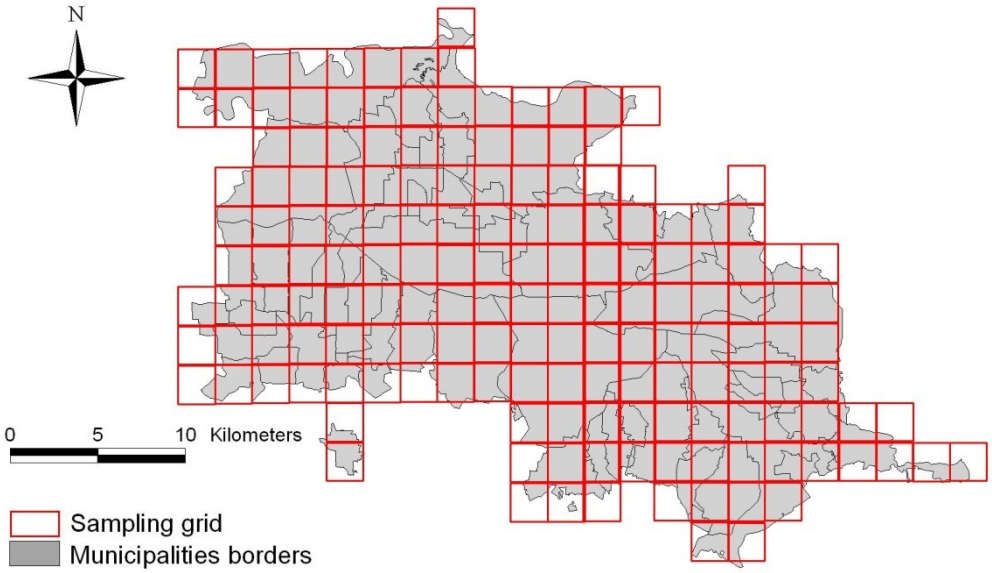


Fig.6 – *Distribution of the sampling grid throughout the Agro Aversano*

3.2 Surface soils and soil profiles sampling

Between October 2007 and April 2008 a first sampling of surface soils was carried out. According to the FOREGS sampling procedures (Plant et al., 1996; Salminen et al., 1998) about 1.5 Kg of soil sample has been collected at a depth of 5-15 cm from the surface in each cell. Due to the local morphology and to the high urbanization rate of the area, not all cells could be sampled. At the end of this first sampling phase, a total of 113 topsoils were collected (Fig.6).

A second sampling started in September 2008 in order to collect two soil profiles in the municipalities of Capua and Mariglianella (Fig.7). The soil profiles sampling sites have been chosen after the elaboration and the study of the dot and interpolated maps produced on the basis of the major elements concentrations in the topsoils. The attention has been focused on

two areas characterized by a significantly different land use and in which, Pb and As contents, needed more attention. For each profile a total of 10 samples has been collected, from the surface to 1 m depth (1 sample every 10 cm).

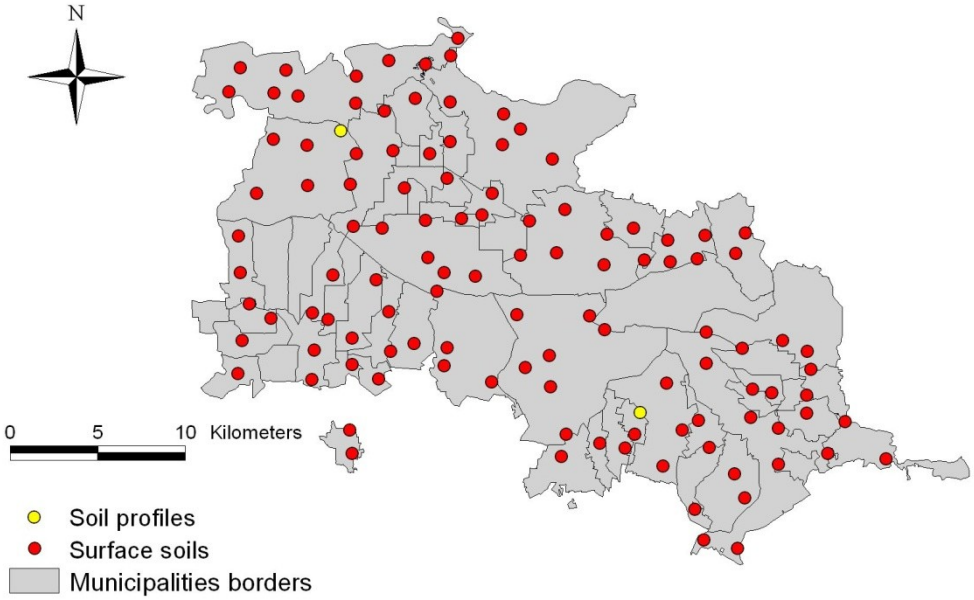


Fig.7 – *Surface soils and soil profiles sampling sites*

3.3 Surface waters and groundwaters sampling

In January 2009 stream waters and groundwaters sampling was carried out. Stream waters have been sampled along the Regi Lagni artificial channels by collecting two polypropylene bottles (1 l and 50 ml) in 11 sites (Fig.8).

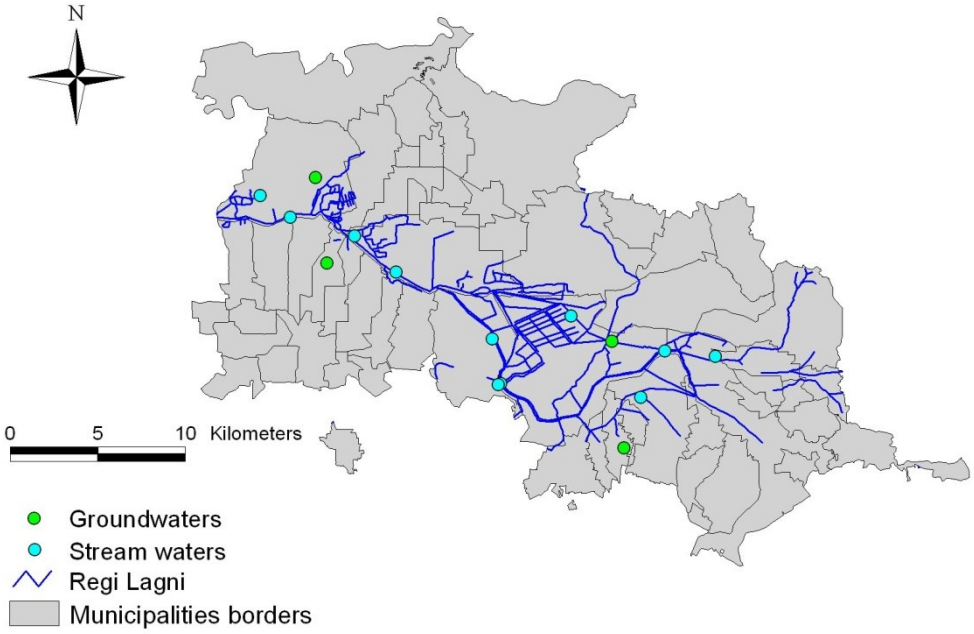


Fig.8 – *Stream waters and groundwaters sampling sites*

The water sampling has been made trying to collect the running water in the middle part of the stream after a three times rinse of the bottles with the stream water itself. The smallest bottles were collected for chemical analysis, the biggest ones were sent to the USGS Radiogenic Isotope Laboratories (Reston, VA) for Pb isotope studies. In the same period 4 groundwater samples (1 liter polypropylene bottle in each site) have been collected in farms, dairies and country houses of the investigated area.

4 Methodologies

4.1 Sample preparation and chemical analysis

Surface soils

After being dried with infra-red lamps at a temperature constantly kept below 35°C, the 113 surface soils, have been pulverized in a ceramic mortar and then sieved at the < 100 mesh fraction (150 μm). The obtained pulps have been stored in small plastic bags containing at least 30 g of samples, and then shipped to the ACME Analytical Laboratories Ltd (Vancouver, Canada), accredited under ISO 9002. They have been analyzed by ICP-MS technique after aqua regia digestion (Cicchella et al. 2008), for the determination of the following 53 elements: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr. The aqua regia attack is considered to be one of the best total dissolution processes: it dissolves metals in water soluble salts, in cation-exchange sites, in clay particles, in organic chelates, in amorphous Mn and Fe oxides and hydroxides, in carbonates, in sulphides and in some sulphates. Aqua regia also partially solubilizes metals in ferromagnesian-rich silicates and some Fe, Ti and Cr oxides. The most resistant minerals to this kind of attack are the Ta, Hf, Zr, Nb and Ba sulphates.

In the Lab about 15 g-split of each powdered soil sample were digested in 45 ml of aqua regia (2:2:2 of $HCl:HNO_3:H_2O$) at 95° C for about one hour; the obtained solution was then taken to a final volume of 300 ml with 5% HCl. Aliquots of sample solution were aspirated into a Perkin Elmer Elan 6000 ICP-mass spectrometer.

In Table 1 the instrumental detection limits (DL) for each element are reported.

On 53 analyzed elements, 5 had to be deleted from the database (Ge, In, Ta, Re, Pd) because of their concentrations below the detection limit in most of the samples. For all those elements with concentrations below detection limit only for few samples, a conventional substitution of the non registered value with an assigned value corresponding to 50% of the detection limit, has been applied.

Stream waters

To avoid absorption or precipitation problems, the 11 stream water samples (50 ml bottles), once in the University of Naples laboratories, have been acidified to pH < 2 using ultra pure nitric acid. Then, these samples have been shipped to the ACME Labs to be analyzed by ICP-MS using the 2CB full suite Acme's package for the determination of 72 elements (Ag, Al, As, Au, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, S, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr). Due to the strict detection limits of water analysis, among these 72 elements, 17 (Ag, Au, Bi, Ge, Hf, Hg, In, Ir, Os, Pd, Pt, Rh, Ru, Ta, Te, Th) could not be measured for all or for at least 5 of the 11 submitted samples and, therefore, could not be studied.

Detection limits for this kind of analysis on water samples are reported in Table 2.

Table 1. *Instrumental Detection Limits (DL) for ICP-MS analysis on soils by ACME Analytical Lab*

ELEMENT	UNIT	DL	ELEMENT	UNIT	DL	ELEMENT	UNIT	DL
Ag	µg/kg	2	Hf	mg/kg	0.02	S	%	0.02
Al	%	0.01	Hg	µg/kg	5	Sb	mg/kg	0.02
As	mg/kg	0.1	In	mg/kg	0.02	Sc	mg/kg	0.1
Au	µg/kg	0.2	K	%	0.01	Se	mg/kg	0.1
B	mg/kg	20	La	mg/kg	0.5	Sn	mg/kg	0.1
Ba	mg/kg	0.5	Li	mg/kg	0.1	Sr	mg/kg	0.5
Be	mg/kg	0.1	Mg	%	0.01	Ta	mg/kg	0.05
Bi	mg/kg	0.02	Mn	mg/kg	1	Te	mg/kg	0.02
Ca	%	0.01	Mo	mg/kg	0.01	Th	mg/kg	0.1
Cd	mg/kg	0.01	Na	%	0.001	Ti	%	0.001
Ce	mg/kg	0.1	Nb	mg/kg	0.02	Tl	mg/kg	0.02
Co	mg/kg	0.1	Ni	mg/kg	0.1	U	mg/kg	0.1
Cr	mg/kg	0.5	P	%	0.001	V	mg/kg	2
Cs	mg/kg	0.02	Pb	mg/kg	0.01	W	mg/kg	0.1
Cu	mg/kg	0.01	Pd	µg/kg	10	Y	mg/kg	0.01
Fe	%	0.01	Pt	µg/kg	2	Zn	mg/kg	0.1
Ga	mg/kg	0.1	Rb	mg/kg	0.1	Zr	mg/kg	0.1
Ge	mg/kg	0.1	Re	µg/kg	1			

Table 2. *Instrumental Detection Limits (DL) for ICP-MS analysis on waters by ACME Analytical Lab*

ELEMENT	UNIT	DL	ELEMENT	UNIT	DL	ELEMENT	UNIT	DL
Ag	µg/kg	0.05	Hf	µg/kg	0.02	S	mg/kg	1
Al	µg/kg	1	Hg	µg/kg	0.1	Sb	µg/kg	0.05
As	µg/kg	0.5	Ho	µg/kg	0.01	Sc	µg/kg	1
Au	µg/kg	0.05	In	µg/kg	0.01	Se	µg/kg	0.5
B	µg/kg	5	K	µg/kg	50	Si	µg/kg	40
Ba	µg/kg	0.05	La	µg/kg	0.01	Sm	µg/kg	0.02
Be	µg/kg	0.05	Li	µg/kg	0.1	Sn	µg/kg	0.05
Bi	µg/kg	0.05	Lu	µg/kg	0.01	Sr	µg/kg	0.01
Br	µg/kg	5	Mg	µg/kg	50	Ta	µg/kg	0.02
Ca	µg/kg	50	Mn	µg/kg	0.05	Tb	µg/kg	0.01
Cd	µg/kg	0.05	Mo	µg/kg	0.1	Te	µg/kg	0.05
Ce	µg/kg	0.01	Na	µg/kg	50	Th	µg/kg	0.05
Cl	mg/kg	1	Nb	µg/kg	0.01	Ti	µg/kg	10
Co	µg/kg	0.02	Nd	µg/kg	0.01	Tl	µg/kg	0.01
Cr	µg/kg	0.5	Ni	µg/kg	0.2	Tm	µg/kg	0.01
Cs	µg/kg	0.01	P	µg/kg	20	U	µg/kg	0.02
Cu	µg/kg	0.1	Pb	µg/kg	0.1	V	µg/kg	0.2
Dy	µg/kg	0.01	Pd	µg/kg	0.2	W	µg/kg	0.02
Er	µg/kg	0.01	Pr	µg/kg	0.01	Y	µg/kg	0.01
Eu	µg/kg	0.01	Pt	µg/kg	0.01	Yb	µg/kg	0.01
Fe	µg/kg	10	Rb	µg/kg	0.01	Zn	µg/kg	0.5
Ga	µg/kg	0.05	Re	µg/kg	0.01	Zr	µg/kg	0.02
Gd	µg/kg	0.01	Rh	µg/kg	0.01			
Ge	µg/kg	0.05	Ru	µg/kg	0.05			

4.1.1 Quality controls

In order to process only those data that have an good analytical value, quality controls on the laboratories data have been applied.

Tables 3 and 4 list the accuracy and precision values of the Agro Aversano sample's geochemical data, after the application of the chosen analytical technique.

Accuracy

Accuracy is defined as the degree of closeness of the measurement of a quantity to its true value. The laboratory accuracy error has been determined using the formula:

$$A(\%) = \left(\frac{|X - TV|}{TV}\right) * 100$$

with: X= laboratory's analysis result for the standard sample,

TV= true value of the standard sample.

For the measurement of the analysis accuracy error, Acme's in-house reference materials have been used: for soil samples the standard was DS7, for stream water samples the reference material was the Standard Wastewater D7.

Acceptable accuracy error values don't have to be over 15%.

In soil analysis 4 elements (Hf, La, Sb, Y) have an accuracy error over 15%, in water analysis none of the element exceed this acceptability limit.

Precision

Precision is defined as the degree of reproducibility of a measurement; in other words is the degree of how, repeated measurements, show the same results under the same conditions. The precision has been calculated as relative percentage difference (%RPD) using the formula:

$$\%RPD = \left[\frac{|SV - DV|}{((SV + DV)/2)}\right] * 100$$

with: SV= original sample value,

DV= duplicate sample value.

Precision of the performed analysis, has been calculated on 6 in-house replicates and one blind duplicate for soils, and on one in-house replicate for waters.

Values can be considered good if the RPD is < 35% for soils and < 20% for waters.

In soils the relative percentage difference (%RPD) is more than 35% only for Te; in water analysis none of the elements exceed the limit of 20%.

Table 3. *Accuracy error and precision of the soil data*

Elements	Unit	Accuracy error (%)	Precision (%RPD)
Ag	µg/kg	7.3	16.1
Al	%	9.5	2.0
As	mg/kg	8.3	6.8
Au	µg/kg	5.9	11.3
B	mg/kg	6.7	18.5
Ba	mg/kg	3.8	7.3
Be	mg/kg	8.8	5.7
Bi	mg/kg	8.3	5.2
Ca	%	5.2	3.2
Cd	mg/kg	4.8	7.9
Ce	mg/kg	5.5	2.3
Co	mg/kg	3.1	4.2
Cr	mg/kg	14.0	7.1
Cs	mg/kg	3.0	3.7
Cu	mg/kg	3.4	3.6
Fe	%	3.2	2.7
Ga	mg/kg	7.0	5.1
Hf	mg/kg	16.4	11.1
Hg	µg/kg	4.5	12.8
K	%	5.5	10.3
La	mg/kg	20.0	4.9
Li	mg/kg	8.1	3.7
Mg	%	3.8	3.8
Mn	mg/kg	4.6	4.3
Mo	mg/kg	3.8	4.6
Na	%	3.8	8.5
Nb	mg/kg	11.0	10.5
Ni	mg/kg	2.9	5.2
P	%	6.0	5.4
Pb	mg/kg	7.2	9.5
Pt	µg/kg	7.6	34.7
Rb	mg/kg	4.5	6.2
S	%	4.2	0.0
Sb	mg/kg	28.8	10.5
Sc	mg/kg	12.8	6.3
Se	mg/kg	4.6	28.3
Sn	mg/kg	5.2	5.5
Sr	mg/kg	7.7	3.2
Te	mg/kg	8.3	43.3
Th	mg/kg	8.6	3.3
Ti	%	5.5	7.1
Tl	mg/kg	4.3	4.5
U	mg/kg	8.2	2.7
V	mg/kg	5.0	3.9
W	mg/kg	10.0	9.2
Y	mg/kg	22.5	4.4
Zn	mg/kg	4.0	5.5
Zr	mg/kg	8.9	11.0

Table 4. *Accuracy error and precision of the water data*

Elements	Unit	Accuracy error (%)	Precision (%RPD)
Al	µg/l	4.9	4.8
As	µg/l	3.3	3.4
Ba	µg/l	3.0	3.0
Be	µg/l	13.0	13.9
Cd	µg/l	0.2	0.2
Co	µg/l	9.0	9.5
Cr	µg/l	9.7	10.2
Cu	µg/l	9.8	10.3
Fe	µg/l	4.4	4.3
Mn	µg/l	5.4	5.5
Mo	µg/l	3.0	3.1
Ni	µg/l	6.6	6.9
Pb	µg/l	4.9	4.8
Sb	µg/l	0.9	0.9
Se	µg/l	2.3	2.3
Sr	µg/l	12.8	13.6
Tl	µg/l	2.1	2.1
V	µg/l	11.9	12.6
Zn	µg/l	5.1	5.2

4.2 Sample preparation for Pb isotopes analysis

Surface soils and soil profiles

The 20 soil profiles, after the collection, have been sent to the USGS Laboratories in Reston (VA, USA). Here the samples have been air-dried and sieved at < 60 mesh fraction (250 µm). In order to determine whether the content of metals in soils is mainly due to anthropic or geogenic contribution, a leaching procedure has been applied to them. The acid

mixture used for this is a 1.5N HCl+3N HNO_3 solution, which preferentially dissolves amorphous Fe- and Mn-oxyhydroxides, whose coatings are considered to catch most of the anthropogenic Pb. About 200 mg of each sample have been leached with 3 ml of the acid solution, placed in an ultrasonic bath and centrifuged for 5 minutes. The product of this operation are two fractions of the same sample inside the tube: one liquid (leached, L), and one at the bottom of the tube in a solid state (residue, R). The residue samples have been directly placed on warm hot plates to dry at < 50°C while, the leached portion of the soils have been first digested in an Ethos Plus Microwave Lab Station for 15 minutes and then put to dry (Fig. 9).

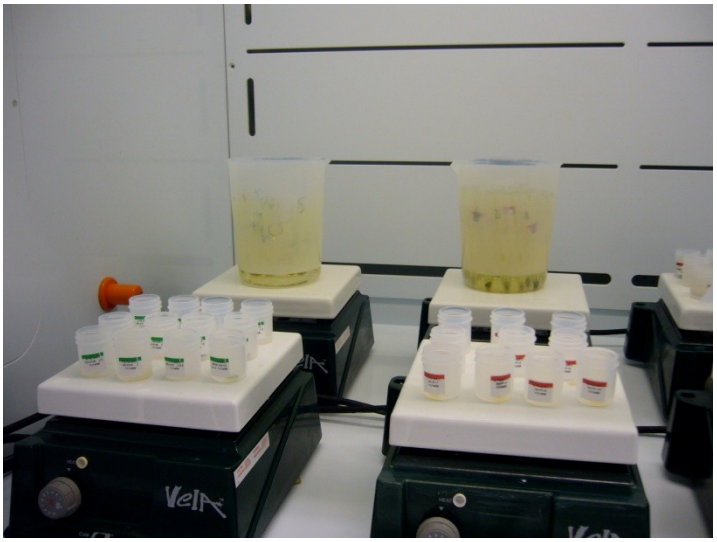


Fig. 9 – *Residue and leached samples drying on hot plates*

Once dry, the samples have been processed and evaporated using a multistep chemistry procedure with different amount of concentrated HNO_3, concentrated HF, 4N HCl and 0.5N HBr. In order to separate Pb, samples were finally passed through Pb exchange columns by using an anion-exchange resin, 0.5N HNO_3 and 0.5N HBr (Ayuso et al., 2004) (Fig. 10).

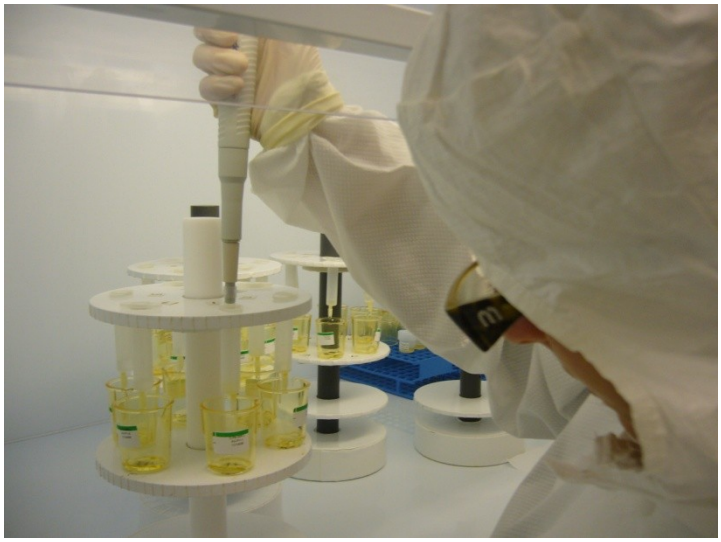


Fig. 10 - *Lead exchange columns*

In order to ensure the maximum purity of the extracted Pb, the step of the exchange columns has been made twice.

The entire procedure has been applied to the 20 duplicate samples of surface soils too.

Stream waters and groundwaters

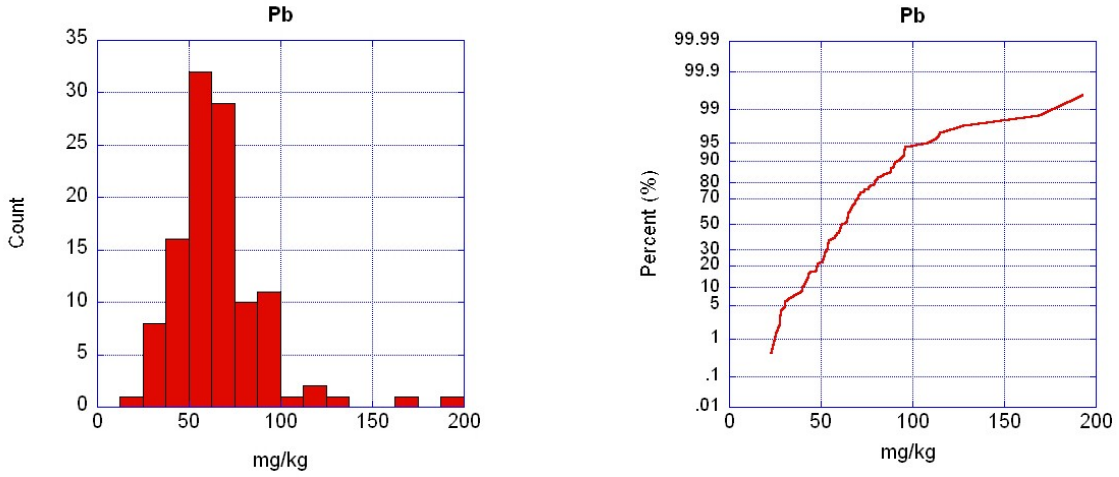
The 15 water samples (11 stream waters and 4 groundwaters in 1 l bottles) have been filtered using 100 micropore cellulose filters with an opening space of 0.4 μm. After the filtration they have been dried on warm hot plates (T < 50°C) and then processed through the same Pb chemistry and Pb elution protocol used for surface soils and soil profiles.

4.3 Geochemical data elaboration

4.3.1 Univariate statistics

A traditional statistical analysis of the soils analytical data (Sinclair, 1976), was performed by using the KaleidaGraph 4.0 program.

The distribution of the elemental concentrations for all the 113 soil samples has been plotted using histograms and cumulative frequency curves (Fig.11a-11b).



(a) **(b)**

Fig.11 – *Histogram (a) and cumulative frequency curve (b) for Pb*

Due to the small number of water samples collected, it wasn't possible to make an appropriate statistic elaboration for them too.

4.3.2 Geochemical map production

Data obtained from the ICP-MS analysis on surface soils, have been processed through the ArcView GIS 3.2 software for map elaboration. According to the detection limits for each element, a total of 48 topsoil dot maps were produced. Dot maps report the real concentration of each element site by site, with the dot radius depending on the element concentration, and classified by a cumulative frequency graph. In addition to this, interpolated maps reporting the expected element's content in non sampled areas, were realized by using the Multifractal Inverse Distance Weighted (MIDW) method (Cheng, 1999) available in the software GeoDAS (Cheng, 2003). Data interpolation has been realized using a search distance of 1 Km and a map resolution of 150 m (Cheng, 200; Lima et al., 2003a; Cicchella et al., 2005). Dot maps were then plotted on interpolated maps, thus giving a complete picture of elemental concentrations in the investigated area.

4.3.3 Factor analysis in R-Mode

Factor analysis is a statistical method used to group the information of a certain amount of chemical elements with similar geochemical patterns. This method is based on the concept of communality, defined as the common variance explained by the factors, for each variable. To simplify the interpretation of the results, an orthogonal rotation (varimax rotation) that minimizes the number of variables with high loading on each factor, is applied (Reimann et al., 2002).

R-mode factor analysis has been performed using SPSS software on a matrix containing 24 elements. The elements with a with loading higher than 0.5 are considered as representative members of each association that results from the chosen factor model.

A total of three factor scores maps have been realized using the following elemental associations:

- **F1**: K, Sr, Rb, V, Na, P, Co, Ba, Cu, Tl, U;
- **F2**: La, Th, Be, Ga, Ti, As, U, Tl (-Ca);
- **F3**: Sn, Hg, Pb, Sb, Ag, Zn.

The factor association F1 (K, Sr, Rb, V, Na, P, Co, Ba, Cu, Tl, U) is made up by elements that characterize the Neapolitan Volcanic Province, especially alkaline (Na, K, Rb) and earth-alkaline (Ba, Sr) metals.

The association F2 (La, Th, Be, Ga, Ti, As, U, Tl (-Ca)) accounts is characterized by the presence of a negative factor score value, the one related to the calcium (-0.701), whose low correlation could be the evidence of non carbonatic bedrock lithologies. This factor association, includes, besides all the metals and non metals, three elements of lanthanide and actinide series (La, Th, U).

The association F3 (Sn, Hg, Pb, Sb, Ag, Zn) includes all those elements thought to be characteristics of anthropic contaminations. Except Ag, all the others belong to the group of elements, whose concentration limits into soils, have been fixed by the Italian Environmental Law 152/06.

4.4 Pb isotopes analysis

4.4.1 Pb isotopes

Lead has four stable isotopes: ^{208}Pb, ^{207}Pb, ^{206}Pb and ^{204}Pb; three of them (^{208}Pb, ^{207}Pb, ^{206}Pb) derive from radioactive decay of ^{232}Th (^{208}Pb), ^{235}U (^{207}Pb) and ^{238}U (^{206}Pb), while the ^{204}Pb isotope is the only one non radiogenic. Each natural material has its own characteristic Pb isotope ratio which is the result of the different half-lives of Th and U and the primordial U/Th/Pb availability in that material. During geologic eras the combination of these key factors has lead to the production of an isotopic signature for each Earth's reservoir (Faure, 1986; Dickin, 1995; Galer and Goldstein, 1996). Furthermore, environmental and industrial processes do not fractionate Pb isotopes, and the different materials keep their original source ratios. This isotopic stability makes the Pb isotopes an useful tool to trace contamination sources, both for geologic (natural Pb contents in bedrocks) and anthropic sources (isotopic signature of the ore body in which, Pb for human activities, has been extracted) (Ayuso et al., 2008; Kramers and Tolstikhin, 1997).

4.4.2 Thermo Ionic Mass Spectrometer (TIMS)

Lead isotopic analysis on 20 surface soils, 20 soil profiles, 11 stream waters and 4 groundwaters have been run in the Radiogenic Isotope Laboratory of the US Geological Survey in Reston, VA. For these analysis a Finnigan-MAT 262 Thermal Ionization Mass Spectrometer (TIMS) with a Faraday multi-collector cup, was used (Fig.12).

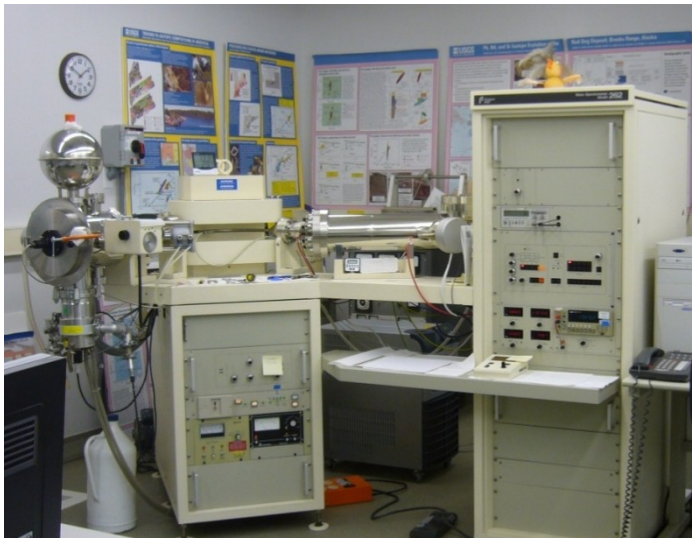


Fig.12 – *Finnigan-MAT 262 Thermal Ionization Mass Spectrometer (TIMS)*

The Pb collected through all the chemistry and elution procedures for each soil sample, has been loaded on a single post Re degassed filament by using the method of silica gel and phosphoric acid. The phosphoric acid's main properties for this application are: displacing all other anion species, destroying organic residues and gluing the sample to the filament. Silica gel acts as a blanket over the sample and retards Pb volatilization (Cameron et al., 1969) thus

permitting the heating of the filament until the wanted temperature, without losing the Pb. Filaments have then been loaded on a 13 samples carousel and put into the turret position of the TIMS. Once in the machine, under high vacuum condition, high voltage has passed through the filament which slowly and gradually heated until an evaporation value of 1800 mA. Through heating, the sample, has been atomized and ionized and a stable ion beam formed. The beam, accelerated by the electrical potential gradient, was focused by a series of slits and electrostatically charged plates and directed through a big magnet. The magnetic field separated the initial ion beam into different beams on the basis of their mass to charge ratio; these beams finally reached the collectors where, were converted into voltage and, through the comparison of voltages, lead isotopic ratios were measured.

Isotopic mass fractionation has been constantly monitored by periodic analysis of a standard (NIST-SRM981). The obtained isotopic ratios were corrected for mass fractionation relative to this standard.

5 Results and discussion

5a Statistical data

The main statistical parameters (minimum value, maximum value, mean, median and standard deviation) of the data obtained from the ICP-MS analysis on both soils and waters, are reported respectively in Table 5 and in Table 6.

Table 5. *Statistical parameters of the 113 surface soils analyzed*

Element	Unit	Minimum	Maximum	Mean	Median	Std deviation
Ag	µg/kg	21	424	111	92	77
Al	%	1.90	8.27	4.91	5.16	1.33
As	mg/kg	5.60	25.60	13.14	13.00	3.53
Au	µg/kg	2.3	44.8	14.5	11.7	8.5
B	mg/kg	6.0	54.0	16.4	13.0	9.3
Ba	mg/kg	120	833	406	391	162
Be	mg/kg	1.80	9.70	5.42	5.70	1.46
Bi	mg/kg	0.220	1.170	0.457	0.450	0.128
Ca	%	0.53	19.36	3.96	2.35	3.99
Cd	mg/kg	0.100	1.450	0.448	0.400	0.211
Ce	mg/kg	32	134	86	88	19
Co	mg/kg	2.80	16.90	9.89	9.00	3.40
Cr	mg/kg	1.80	45.40	13.63	12.10	6.89
Cs	mg/kg	3.07	20.43	13.28	14.01	4.13
Cu	mg/kg	9	677	109	69	116
Fe	%	1.13	3.55	2.54	2.53	0.56
Ga	mg/kg	3.80	15.00	9.50	10.00	2.34
Hf	mg/kg	0.100	1.690	0.452	0.370	0.274
Hg	µg/kg	13	410	91	62	78
K	%	0.29	4.53	1.51	1.05	1.13
La	mg/kg	16.6	63.2	45.1	46.2	9.3
Li	mg/kg	10.4	34.5	22.2	22.5	5.0
Mg	%	0.23	2.14	0.62	0.59	0.24
Mn	mg/kg	291	1391	802	808	182
Mo	mg/kg	0.34	2.58	1.20	1.05	0.52
Na	%	0.024	1.379	0.364	0.225	0.306
Nb	mg/kg	1.38	15.56	8.45	8.93	3.19
Ni	mg/kg	2.1	36.3	13.1	12.7	5.4
P	%	0.026	0.452	0.179	0.158	0.099
Pb	mg/kg	23	193	65	62	25
Pd	µg/kg	5.0	39.0	7.4	5.0	6.5
Pt	µg/kg	1.0	17.0	3.8	3.0	2.7
Rb	mg/kg	49	273	144	130	63
Re	µg/kg	0.500	4.000	0.739	0.500	0.579
S	%	0.010	0.090	0.037	0.040	0.016
Sb	mg/kg	0.220	1.850	0.769	0.660	0.335
Sc	mg/kg	0.80	4.20	2.48	2.50	0.62
Se	mg/kg	0.050	0.900	0.470	0.500	0.237
Sn	mg/kg	1.40	8.80	4.05	3.60	1.53
Sr	mg/kg	64	414	196	180	78
Te	mg/kg	0.010	0.140	0.042	0.040	0.027
Th	mg/kg	2.1	21.4	13.5	13.9	3.9
Ti	%	0.017	0.210	0.143	0.152	0.043
Tl	mg/kg	0.53	3.62	1.93	1.90	0.69
U	mg/kg	0.70	7.60	3.71	3.40	1.56
V	mg/kg	26	142	71	63	28
W	mg/kg	0.30	2.50	1.18	1.20	0.36
Y	mg/kg	6.5	26.7	15.7	15.6	3.3
Zn	mg/kg	34	215	103	96	33
Zr	mg/kg	5.9	131.1	40.8	35.9	22.2

Table 6. *Statistical parameters of the 11 surface waters analyzed*

Element	Unit	Minimum	Maximum	Mean	Median	Std Deviation
Al	µg/kg	91	4171	1045	588	1144
As	µg/kg	1.40	7.50	4.22	4.30	1.76
B	µg/kg	27	247	163	177	64
Ba	µg/kg	24	71	41	38	13
Be	µg/kg	0.025	0.770	0.182	0.100	0.229
Br	µg/kg	53	716	357	377	172
Ca	µg/kg	68528	205952	138704	136833	43461
Cd	µg/kg	0.025	0.210	0.083	0.070	0.060
Ce	µg/kg	0.08	11.85	2.39	1.15	3.32
Cl	mg/kg	21	205	102	97	51
Co	µg/kg	0.220	1.030	0.561	0.570	0.215
Cr	µg/kg	2.8	12.1	7.8	8.6	3.012
Cs	µg/kg	0.350	1.010	0.656	0.650	0.207
Cu	µg/kg	4.6	26.1	11.0	8.2	6.3
Dy	µg/kg	0.005	0.480	0.102	0.050	0.136
Er	µg/kg	0.005	0.250	0.056	0.040	0.068
Eu	µg/kg	0.005	0.150	0.032	0.010	0.043
Fe	µg/kg	34	1583	344	197	453
Ga	µg/kg	0.025	0.530	0.175	0.130	0.138
Gd	µg/kg	0.020	0.710	0.176	0.110	0.190
Ho	µg/kg	0.005	0.090	0.020	0.010	0.024
K	µg/kg	12609	60275	33906	37809	15772
La	µg/kg	0.05	5.62	1.16	0.50	1.59
Li	µg/kg	1.5	18.7	10.3	12.4	5.5
Lu	µg/kg	0.005	0.030	0.011	0.010	0.007
Mg	µg/kg	4988	47557	25092	25954	11719
Mn	µg/kg	34	246	136	141	63
Mo	µg/kg	0.60	14.40	6.17	7.10	4.48
Na	µg/kg	13533	118998	72345	73551	26833
Nb	µg/kg	0.040	0.300	0.162	0.140	0.093
Nd	µg/kg	0.030	4.480	0.928	0.410	1.269
Ni	µg/kg	0.10	4.80	2.05	2.30	1.49
P	µg/kg	152	6634	1599	905	1897
Pb	µg/kg	1.20	6.30	3.06	2.60	1.54
Pr	µg/kg	0.010	1.190	0.249	0.110	0.336
Rb	µg/kg	12	85	48	55	21
Re	µg/kg	0.005	0.040	0.019	0.020	0.012
S	mg/kg	8	141	74	86	47
Sb	µg/kg	0.090	0.740	0.511	0.620	0.234
Sc	µg/kg	3.0	8.0	5.4	5.0	1.2
Se	µg/kg	0.500	4.300	2.791	3.500	1.264
Si	µg/kg	6509	25736	16257	16208	4399
Sm	µg/kg	0.010	0.780	0.160	0.080	0.220
Sn	µg/kg	0.025	1.320	0.336	0.270	0.367
Sr	µg/kg	138	743	464	479	181
Tb	µg/kg	0.005	0.100	0.023	0.010	0.028
Ti	µg/kg	12.0	55.0	25.5	21.0	12.9
Tl	µg/kg	0.010	0.260	0.085	0.080	0.066
Tm	µg/kg	0.005	0.040	0.011	0.010	0.010
U	µg/kg	1	43	18	18	12
V	µg/kg	2.00	13.30	9.43	10.70	3.56
W	µg/kg	0.040	0.580	0.272	0.300	0.180
Y	µg/kg	0.040	2.390	0.534	0.280	0.669
Yb	µg/kg	0.010	0.230	0.065	0.050	0.060
Zn	µg/kg	16	61	38	39	15

Data related to surface soils have been statistically and cartographically elaborated to realize a complete suite of dot and interpolated geochemical maps.

Due to the small amount of water samples collected, it wasn't possible to process their data from ICP-MS analysis to realize statistical studies, neither to produce geochemical maps. In order to compare obtained data, the concentrations of each element at each sampling site, have been plotted on a unique graph (Fig.13). On the vertical axis the values related to all the analyzed elements are reported in a logarithmic scale. The trend of each sample is identified by a characteristic symbol and color, as reported in the legend on the right.

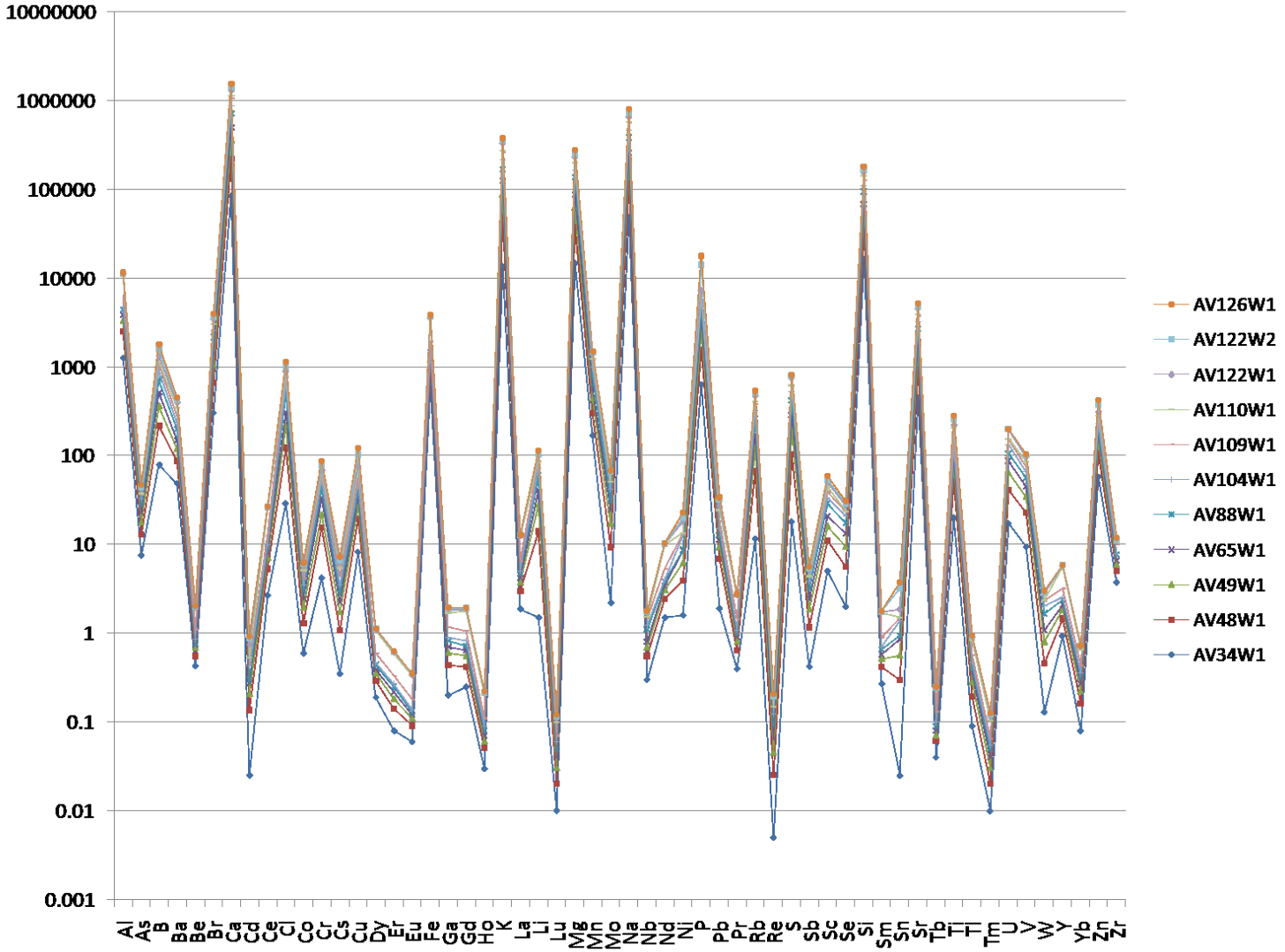


Fig.13 – *Elemental concentrations in stream waters*

5b Geochemical cartography

In recent years the geochemical cartography has been widely used as a powerful tool in different geology branches, from the geochemical exploration to the environmental geochemistry. A geochemical map can be seen as a picture of the health of an investigated area and helps in outlining the main geochemical trends, even at a large scale (De Vivo et al. 2009).

In 1994 the IUGS/IAGC Global Geochemical Baselines Programme established the need of a global geochemical reference baseline for more than 60 elements in different environmental media. In Europe this directive has been carried out by the Forum of European Geological Surveys (FOREGS) which, in 2005 realized the Geochemical Atlas of Europe (Darnley et al., 1995; Salminen et al., 1998, 2005, 2006) by using, in each participating country, standardized sampling methods, analysis and data elaboration (Salminen et al., 1998).

In Italy the first geochemical maps produced, were realized for mining purposes in Calabria, Sardinia, Southern Tuscany and on Peloritani Mountains (De Vivo et al., 1998a, b, c; 2001) by scientists from University of Naples "Federico II", University of Siena and University of Cagliari.

The lack of a National Geological Survey in Italy, forced autonomous researchers groups to realize different scale geological atlases in order to achieve the goal of a complete national geochemical database. Thus, since 2006, a large number of atlases realized on the basis of the FOREGS directives, have been produced: the atlas of the Campania region (De Vivo et al., 2006a), the atlases of Avellino, Salerno, Caserta and Benevento urban areas (Albanese et al., 2007; Cicchella et al., in press; Lima et al.,2007; De Vivo et al., 2006-a; Fedele et al.,2008), and the atlas of Ischia island (Frattini et al., 2006). Furthermore, implementing in southern Italy the sampling accomplished for the Geochemical atlas of Europe, a Geochemical atlas of Italy was produced too (De Vivo et al., 2009).

The geochemical maps realized following these procedures, are a clear and useful tool for local authorities and environmental protection agencies, who need to address the public concerns regarding the toxic element pollution threat to ecosystem and human health. Moreover the atlases are a sound basis for policy makers and help them to face environmental pollution and related legislation with more consciousness.

In the following pages, 30 of the 48 geochemical maps produced on the basis of the Agro Aversano soils analytical results, are shown. All the 48 maps will be part of a forthcoming publication of a geochemical atlas about the whole Domitio-Flegreo Littoral and Agro Aversano area. The 30 maps shown here are those related to the concentrations of the major elements and of all those elements whose concentration limits have been fixed by the 152/06 Italian Environmental Law (Tab.7-8).

Table 7. *Intervention limits for soils as defined by 152/06 Law*

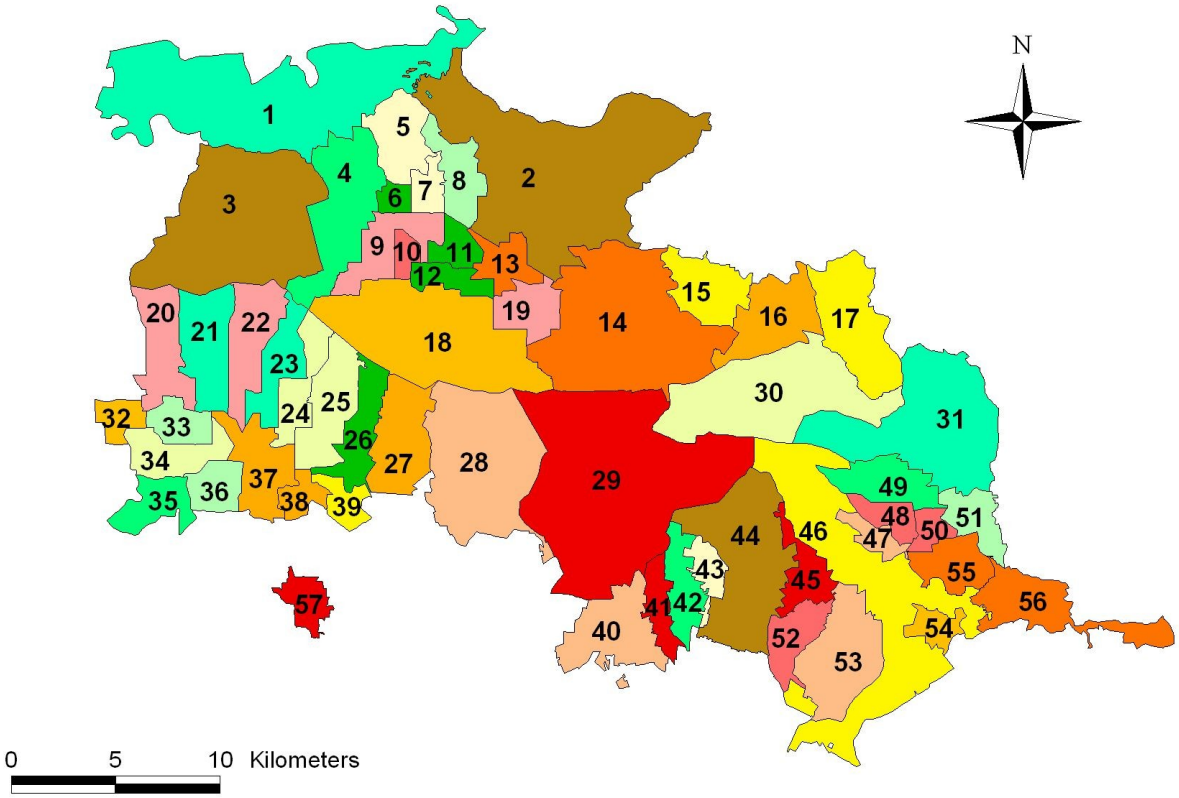
Elements	Residential/recreational intervention limits	Industrial/commercial intervention limit
As	20 mg/kg	50 mg/kg
Be	2 mg/kg	10 mg/kg
Cd	2 mg/kg	15 mg/kg
Co	20 mg/kg	250 mg/kg
Cr	150 mg/kg	800 mg/kg
Cu	120 mg/kg	600 mg/kg
Hg	1 mg/kg	5 mg/kg
Ni	120 mg/kg	500 mg/kg
Pb	100 mg/kg	1000 mg/kg
Sb	10 mg/kg	30 mg/kg
Se	3 mg/kg	15 mg/kg
Sn	1 mg/kg	350 mg/kg
Tl	1 mg/kg	10 mg/kg
V	90 mg/kg	250 mg/kg
Zn	150 mg/kg	1500 mg/kg

Table 8. *Intervention limits for groundwaters as defined by 152/06 Law*

Elements	Groundwaters intervention limit
Ag	10 µg/l
Al	200 µg/l
As	10 µg/l
Be	4 µg/l
Cd	5 µg/l
Co	50 µg/l
Cr	50 µg/l
Cu	1000 µg/l
Fe	200 µg/l
Hg	1 µg/l
Mn	50 µg/l
Ni	20 µg/l
Pb	10 µg/l
Sb	5 µg/l
Se	10 µg/l
Ta	2 µg/l
Zn	3000 µg/l

For each analyzed element there is a brief description of its chemical properties and of its influence on human health (<http://www.lenntech.com/periodic/periodic-chart.htm>); then the related interpolated map, overlaid by a dot one, is shown with its basic statistics graphs (histograms and cumulative frequency curves).

For the sake of maps clear visualization, not all the name of the cited municipalities have been reported. In the next page (Fig.14) is shown a reference map with all their localization.



1	Capua	21	Frignano	41	Castello di Cisterna
2	Caserta	22	Casaluce	42	Brusciano
3	San Tammaro	23	Teverola	43	Mariglianella
4	Santa Maria Capua Vetere	24	Carinaro	44	Marigliano
5	San Prisco	25	Gricignano d'Aversa	45	San Vitaliano
6	Curti	26	Succivo	46	Nola
7	Casapulla	27	Orta d'Atella	47	Cimitile
8	Casagiove	28	Caivano	48	Camposano
9	Macerata Campania	29	Acerra	49	Cicciano
10	Portico di Caserta	30	San Felice a Cancello	50	Comiziano
11	Recale	31	Roccarainola	51	Tufino
12	Capodrise	32	Casapesenna	52	Scisciano
13	San Nicola la Strada	33	San Marcellino	53	Saviano
14	Maddaloni	34	Trentola Ducenta	54	San Paolo Bel Sito
15	Cervino	35	Parete	55	Casamarciano
16	Santa Maria a Vico	36	Lusciano	56	Visciano
17	Arienzo	37	Aversa	57	Melito di Napoli
18	Marcianise	38	Cesa		
19	San Marco Evangelista	39	Sant'Arpino		
20	Villa di Briano	40	Pomigliano d'Arco		

Fig.14 – *Name and localization of all the municipalities of the Agro Aversano*

5b.1 Silver (Ag)

Silver has the highest electrical conductivity of all metals and is an excellent heat conductor.

Silver's main use is as a precious metal, but its salts, especially silver nitrate, are widely used in photography. Other uses are in the electrical and electronic industries and for mirrors and cutlery production. Silver is also used in the electrical industry for the production of printed circuits and computer keyboards. Other applications are in dentistry and in high-capacity zinc long-life batteries.

Silver levels in soils are not usually high except in mineral-rich areas and can be absorbed by plants grown on these kind of soils.

Silver major ores are acanthite, which is mined in Mexico, Bolivia and Honduras, and stephanite, mined in Canada. However, most of the silver, is obtained as a byproduct in the refining of other metals.

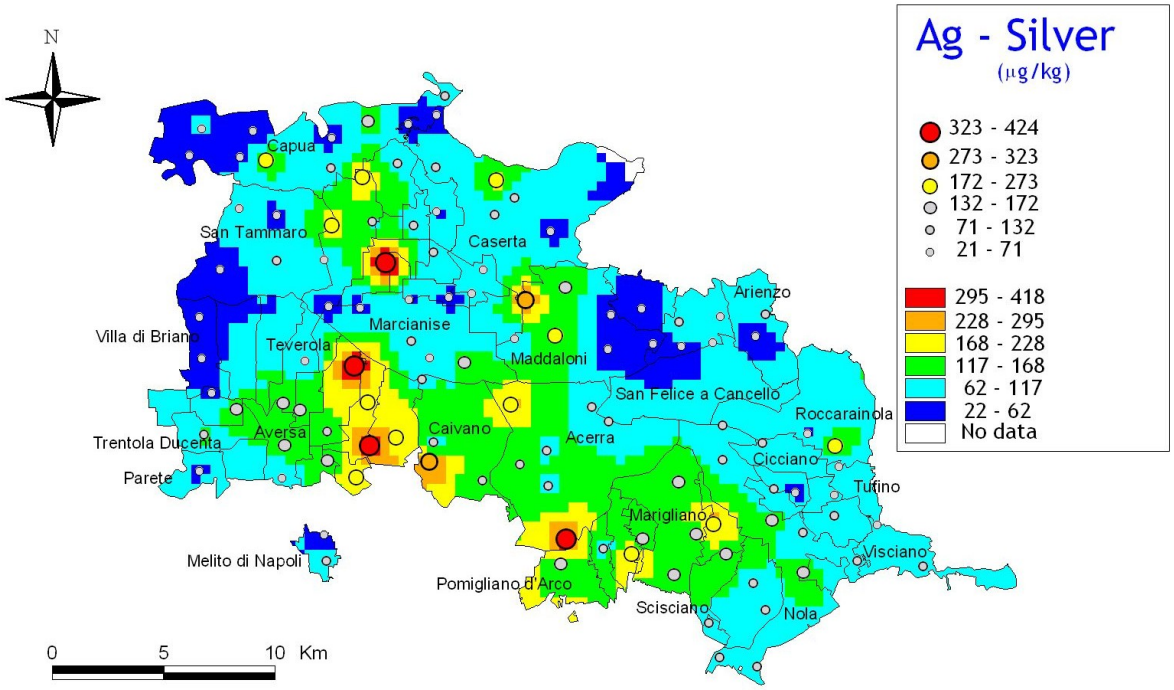
Soluble silver salts, specially $AgNO_3$, are lethal; silver compounds can be slowly absorbed by body tissues, with the consequent bluish or blackish skin pigmentation (argiria). If ingested, silver, is moderately toxic: it may cause stomach problems, nausea, vomiting, diarrhea, and narcosis.

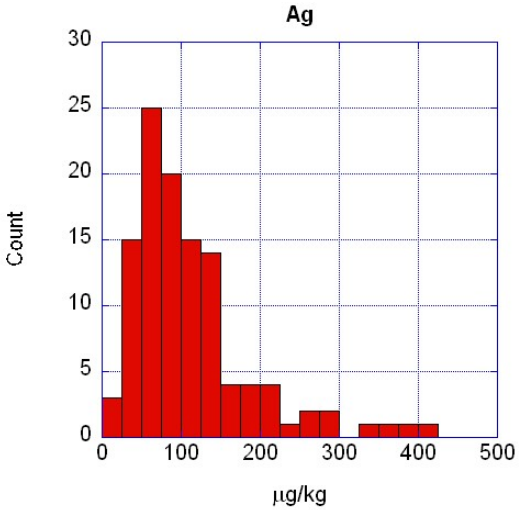
5b.1.1 Distribution of Ag concentrations

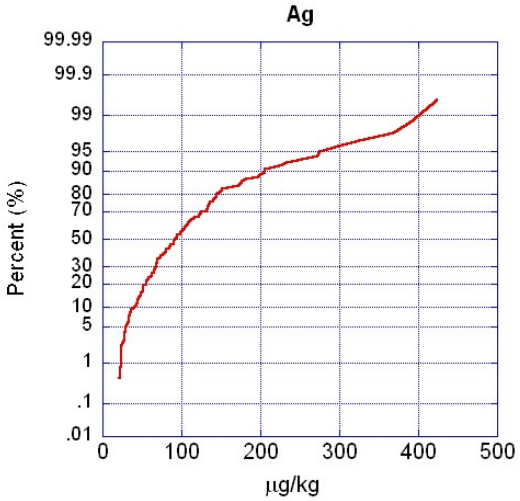
Silver contents in the Agro Aversano range between 21 and 424 μg/kg. Low and very low concentrations (21-132 μg/kg) are found in most of the sampled sites and are distributed throughout the investigated area. In the central southern sector of the Agro Aversano, interpolated values for Ag contents are higher than 117 μg/kg; this sector covers an area that goes from Aversa to San Vitaliano, and to the north reaches Maddaloni town. Similar concentrations are found in the area surrounding the town of Santa Maria Capua Vetere.

The highest values (>323 μg/kg) registered for both dot and interpolated values, are found in the sites sampled in Macerata Campania, to the north of Gricignano d'Aversa, to the south of Orta d'Atella and to the south of Acerra.

Looking at the histogram and at the cumulative frequency curve, there is a quite clear distinction between a major population of data, characterized by lower values, varying between 25 and 225 μg/kg, and samples with anomalously high concentrations, varying from 325 μg/kg up to 425 μg/kg. The most common value registered is included in the range between 50 and 75 μg/kg and is found in 25 soil samples.


N
Ag - Silver
(µg/kg)
323 - 424
273 - 323
172 - 273
132 - 172
71 - 132
21 - 71
295 - 418
228 - 295
168 - 228
117 - 168
62 - 117
22 - 62
No data
Capua
San Tammaro
Caserta
Villa di Briano
Marcianise
Teverola
Maddaloni
Arienzo
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Ag
Count
µg/kg


Ag
Percent (%)
µg/kg

5b.2 Aluminium (Al)

Aluminum is a soft and lightweight metal. It only has one naturally occurring non radioactive isotope, aluminium-27.

Aluminum is found primarily as the ore bauxite and is remarkable for its strength and its light weight. It is widely used in many sectors, from the aerospace industry, to the transportation and building industries. Other applications are mirrors, electrical transmission lines, and packaging (cans, foil, etc.). Pure aluminum easily forms alloys with many elements such as Cu, Zn, Mg, Mn and Si.

Exposure to high Al concentrations, can cause health problems. Its uptake by humans can occur through food, breathing and by skin contact. Long lasting exposures to significant concentrations of aluminum can lead to serious health effects, such as: damage to the central nervous system, dementia, loss of memory, listlessness and severe trembling.

In mines Al can be found dissolved in waters and represents a risk for people working in them. Lung problems (pulmonary fibrosis and lung damage) related to aluminum dust inhalation, may also affect people who work in factories where it's applied in the production process. These problems, known as Shaver's Disease, are emphasized by the presence, in the inhaled air, of silica and oxides of iron. Aluminum may also be implicated in Alzheimer's disease.

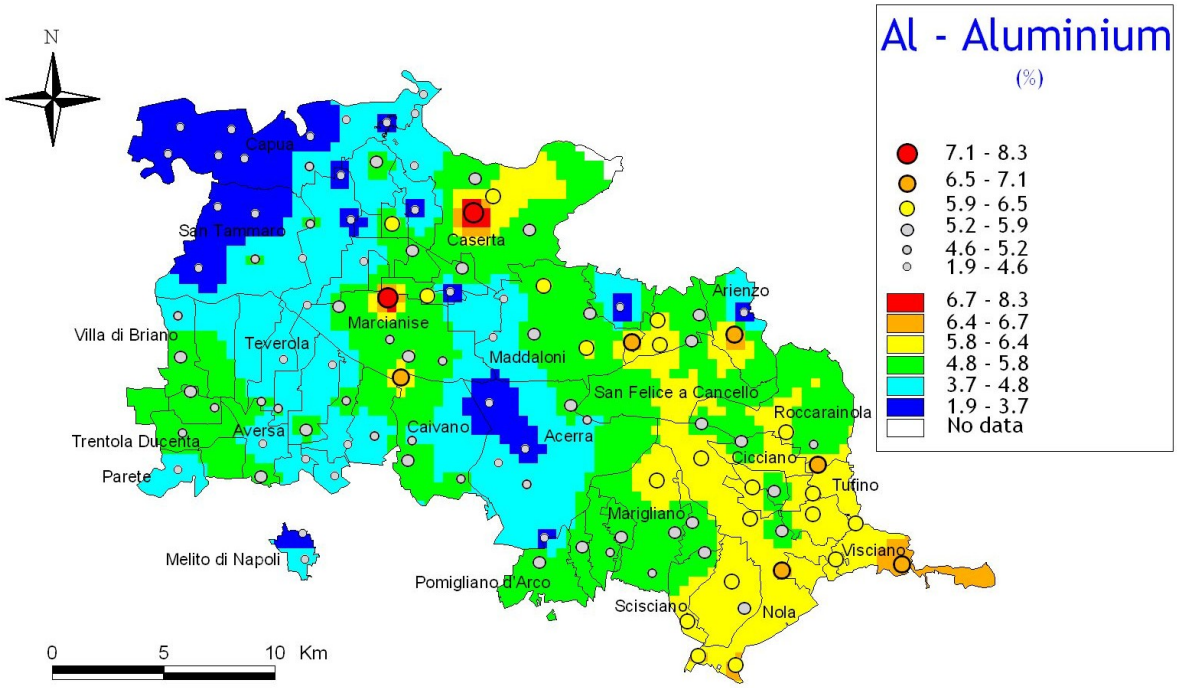
Highest aluminum concentrations in environment are found in acidified lakes; these high contents have a great influence upon the number of fishes and amphibians who lives there (aluminum reacts with proteins in the gills of fish and the embryo's of frogs), but also upon birds and other animals of the biological cycle that consume contaminated fish. Furthermore aluminum ions react with phosphates and causes them to be less available to water organisms. High concentrations of aluminum may not only be found in acidified lakes and air, but also in the groundwater of acidified soils. There are strong indications that aluminum can damage the roots of trees when it is located in groundwater.

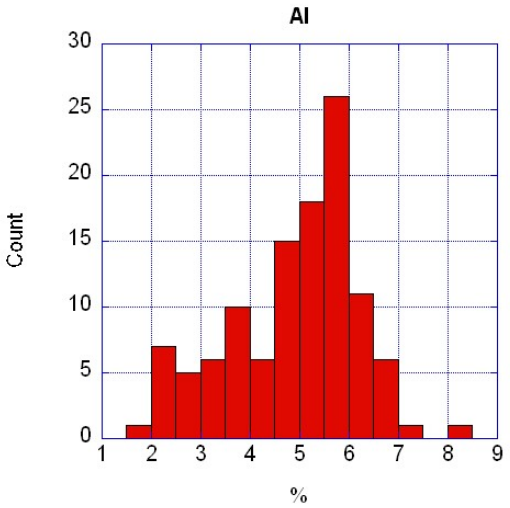
5b.2.1 Distribution of Al concentrations

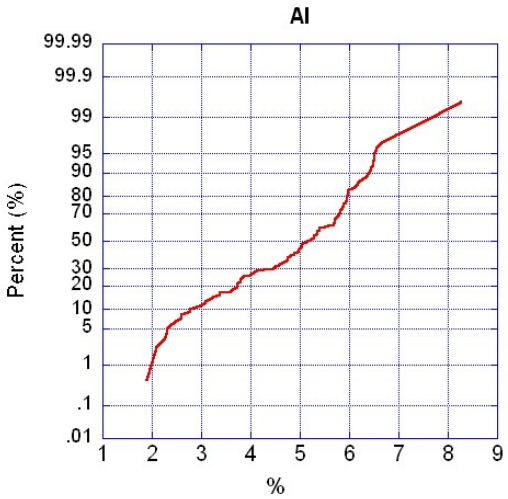
Aluminium concentrations in soils vary from a minimum value of 1.9% to a maximum value of 8.3%. Lowest contents, up to 5.2%, occur in the western sector of the area, from Capua to Aversa, to the borders of Marcianise and Caserta; this range of values also occur in the surroundings of Acerra town, and in very small areas in Melito di Napoli, Arienzo and Cervino. Aluminium contents show an increasing trend moving eastward from Acerra, with values ranging between 5.8% and 6.7% In this range the highest value occur in Visciano; other moderately high contents (6.5%) are found in sites sampled to the east of Nola, and to the south of Roccarainola, the south of Arienzo and the south of Santa Maria a Vico. The highest values (7.1%-8.3%) have been found in Caserta town and to the north of Marcianise. These concentrations seem to be unrelated to the average Al contents of the surrounding areas and, therefore, may be related to local sources of pollution.

The histogram and the cumulative frequency curve produced on the basis of the aluminum concentrations into the analyzed samples, better show the distribution of the values: most of the samples have values varying between 4.5% and 7%, with a peak of 5.5%-

6% for 26 samples. Samples with contents lower than 4.5% don't show a regular statistical distribution, and values over 7% are those that can be considered anomalous.


N
Al - Aluminium
(%)
7.1 - 8.3
6.5 - 7.1
5.9 - 6.5
5.2 - 5.9
4.6 - 5.2
1.9 - 4.6
6.7 - 8.3
6.4 - 6.7
5.8 - 6.4
4.8 - 5.8
3.7 - 4.8
1.9 - 3.7
No data
Capua
San Tammaro
Caserta
Marcianise
Villa di Briano
Teverola
Maddaloni
Arienzo
San Felice a Cancello
Roccarainola
Aversa
Caivano
Acerra
Trentola Ducenta
Parete
Cicciano
Tufino
Marigliano
Visciano
Melito di Napoli
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Al
Count
%


Al
Percent (%)
%

5b.3 Arsenic (As)

Arsenic is a metalloid belonging to the VA group of the periodic table of the elements; it is, at same time, one of the most toxic elements for human beings, but also an ultra-trace micronutrient for both humans and animals.

Arsenic compounds are mainly used as a wood preservative and for the production of special types of glass. In past years arsenic compounds have been widely used for agricultural activities as pesticides, but now are banned in a large number of countries.

It naturally occurs in soils and minerals, especially with sulphur in minerals such as arsenopyrite (AsFeS), realgar, orpiment and enargite. Natural arsenic in the atmosphere comes from volcanoes (about 3000 ton/year) and microorganisms (about 20.000 ton/year), but anthropic arsenic deriving from burning of fossil fuels, is responsible for the highest emission of As in the atmosphere: about 80.000 ton/year.

Arsenic is mainly emitted in the environment by the copper producing industries, but also during lead and zinc production and in agriculture.

Arsenic is an element with a very low water-solubility and that hardly converts to volatile products. Due to human activities, especially mining and melting, naturally immobile arsenics have mobilized and widespread.

Humans may be exposed to arsenic through food, water and air. but also through skin contact with soil or water that contains high arsenic levels. Inorganic arsenic can cause various health effects, such as irritation of the stomach and intestines, decreased production of red and white blood cells, skin changes and lung irritation. Probably the uptake of significant amounts of inorganic arsenic can intensify the chances of cancer development. Inorganic arsenic can also damage DNA. Organic arsenic can cause neither cancer, nor DNA damages, but exposure to high doses may cause certain effects to human health, such as nerve injury and stomachaches. A lethal dose of arsenic oxide is generally about 100 mg.

Arsenic exposure may be higher for people that work with arsenic, for people that live in houses that contain conserved wood of any kind and for those who live on farmlands where arsenic-containing pesticides have been applied in the past.

It cannot be destroyed once it has entered the environment, so that the amounts that we add can spread and cause health effects to humans and animals on many locations on earth and for long periods.

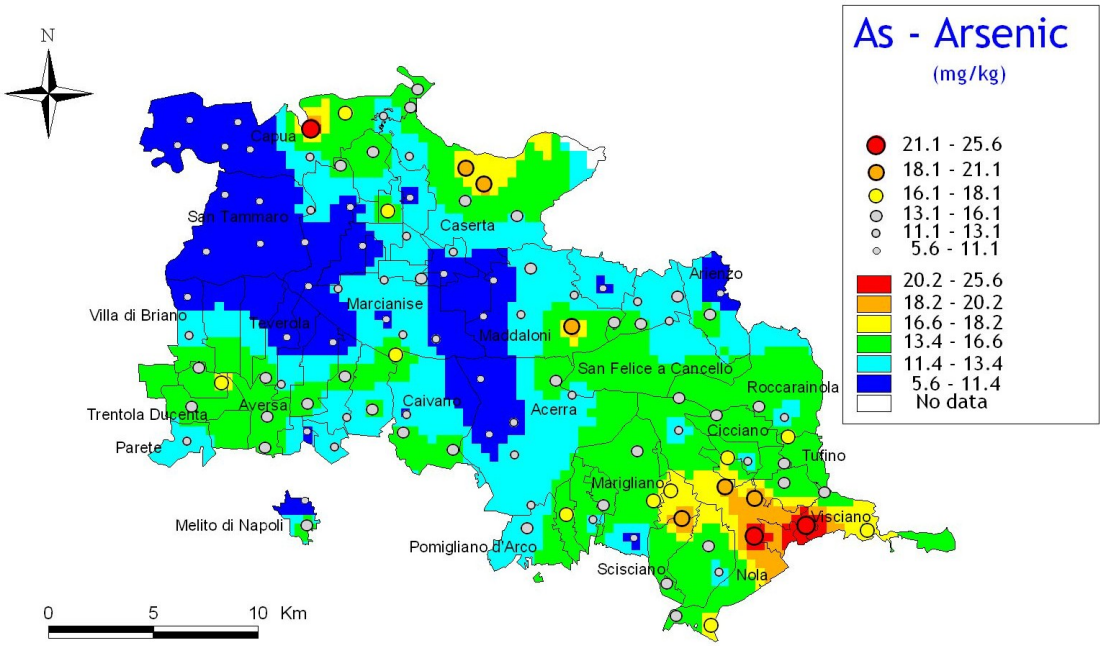
5b.3.1 Distribution of As concentrations

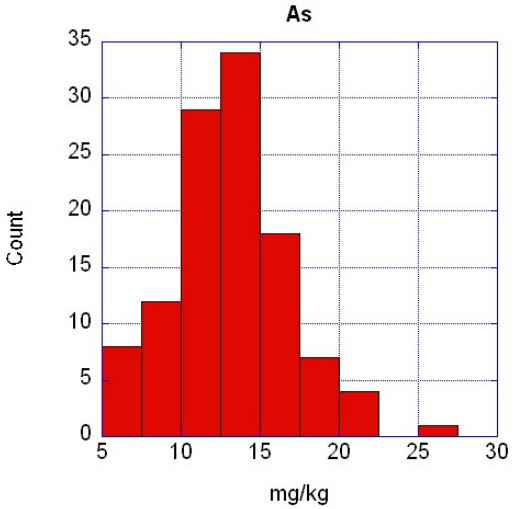
Arsenic contents registered in the Agro Aversano's soils, range from a minimum value of 5.6 mg/kg to a maximum of 25.6 mg/kg. Its distribution map shows an area in which concentrations are low and very low (5.6-13.4 mg/Kg) that extends from San Tammaro and Capua to Maddaloni, and Acerra, and, in the upper eastern part of the Agro Aversano, reaches the municipality of Arienzo. This area, according to the land use, is the one with more developed agricultural activities and is, therefore, the area in which high As concentrations were expected, mainly related to the wide use of arsenical pesticides in the last decades. Arsenic contents gradually and almost homogeneously increase from Scisciano toward Nola and Visciano, with values that go from 18.1 mg/kg to 25.6 mg/kg; the highest contents of this

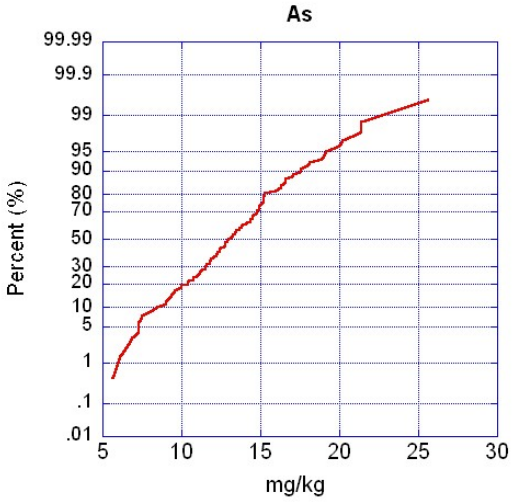
area are found in two sampling sites, one located in Nola and one in Visciano. Values higher than 18.1 mg/kg have also been registered to the north of Caserta town and in eastern Maddaloni, while an anomalously high As content is found to the north of Capua, near the Volturno river.

The statistical graphs realized for As concentrations, show how, its distribution, reflects the presence of only one population of data. Up to 34 samples have a value comprised between 12.5 mg/kg and 15 mg/kg, and other 29 samples have values between 10 mg/kg and 12.5 mg/kg. The highest As concentration (>25mg/kg) is the one outlier of this distribution.

Arsenic is one of the elements for which, the Italian 152/06 Environmental Law, determined the concentration limit for both industrial and residential areas. The first limit is fixed at 50 mg/kg and, in the Agro Aversano's soils samples, is never reached; the residential limit is fixed at 20 mg/kg, and is reached in 5 of the 113 collected samples.


N
As - Arsenic
(mg/kg)
21.1 - 25.6
18.1 - 21.1
16.1 - 18.1
13.1 - 16.1
11.1 - 13.1
5.6 - 11.1
20.2 - 25.6
18.2 - 20.2
16.6 - 18.2
13.4 - 16.6
11.4 - 13.4
5.6 - 11.4
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Maddaloni
Trentola Ducenta
Aversa
Caivano
Acerra
San Felice a Cancello
Roccarainola
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Pomigliano d'Arco
Scisciano
Nola
Visciano
0
5
10 Km


As
Count
mg/kg


As
Percent (%)
mg/kg

5b.4 Beryllium (Be)

Beryllium is a toxic bivalent element, with an excellent thermal conductivity; it's nonmagnetic and air oxidation resistant.

Its main uses are in beryllium-copper alloys for defense and aerospace industries, in the diagnostic X-ray detection, and in computer components production.

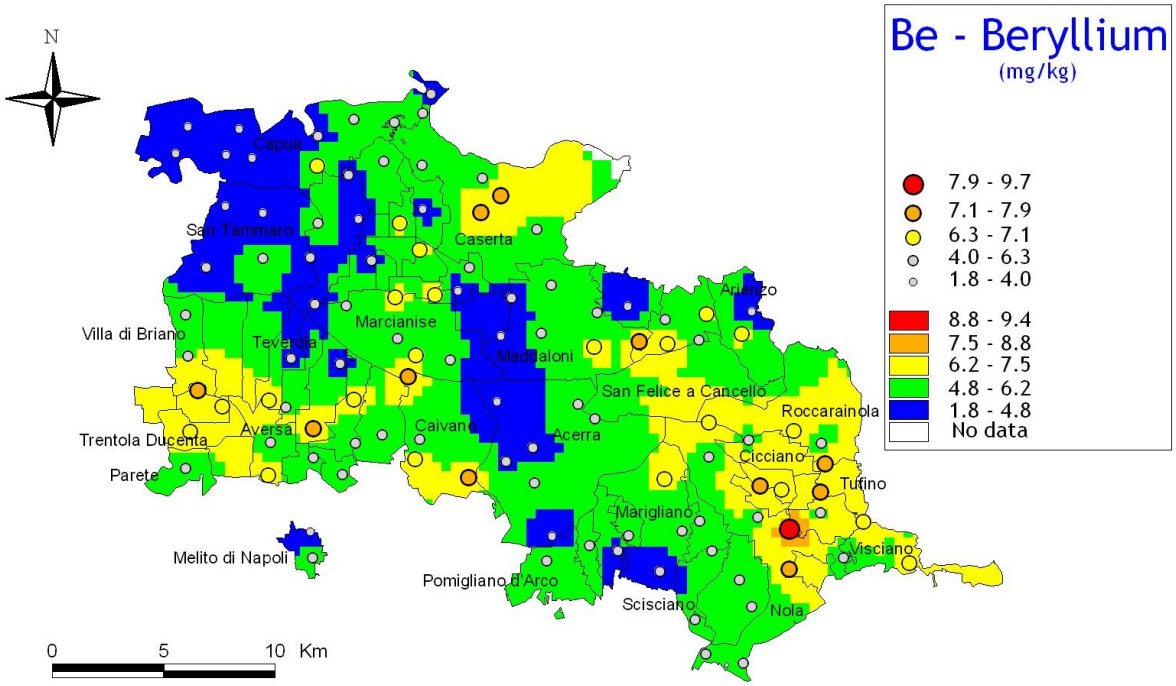
Beryllium average content in soil is 6 mg/kg; in this environmental media it's in a soluble form and can be taken from plants growing on Be-rich soils. Plants could accumulate Be contents varying between 1 and 40 μg/kg; these concentrations are too low to cause health problems to animals who eat these plants.

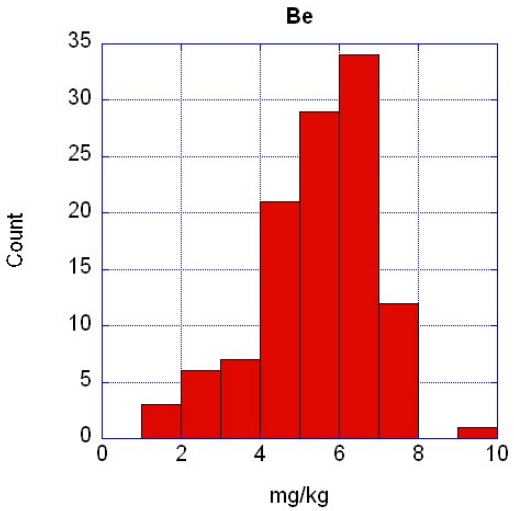
Beryllium added into the environment by anthropic activities is especially by industrial emissions and wastewaters disposals. In waters, through reactions, beryllium becomes insoluble and causes much less harm to organisms than water-soluble form.

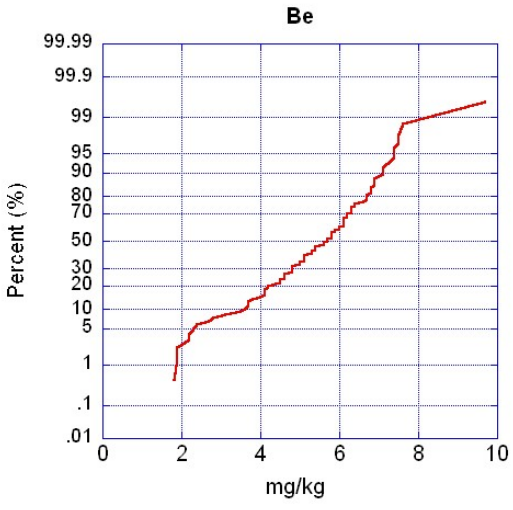
5b.4.1 Distribution of Be concentrations

Beryllium concentrations measured in the soils of the Agro Aversano, range from 1.8 mg/kg to 9.7 mg/kg. Distributions seem to follow any regular pattern; slight differences can be observed between the western (1.8-4.8 mg/kg) and the eastern sector (6.2-7.5 mg/kg) of the studied area. The point in which the highest Be value has been registered is in Nola municipality and is about 9.7 mg/kg.

According to the Italian Environmental Law, beryllium concentrations in soils of industrial areas should not exceed 10 mg/kg, in soils of residential areas this limit is fixed at 2 mg/kg. Looking at both histogram and cumulative frequency curve, it's clear that the limit for the areas with residential destination, is exceeded in almost all the sites in which soil samples have been collected, except in three of them, whose values are, in any case, always higher than 1.8 mg/kg that is the lowest Be concentration registered in all the investigated area.


N
Be - Beryllium
(mg/kg)
7.9 - 9.7
7.1 - 7.9
6.3 - 7.1
4.0 - 6.3
1.8 - 4.0
8.8 - 9.4
7.5 - 8.8
6.2 - 7.5
4.8 - 6.2
1.8 - 4.8
No data
Capua
San Tammaro
Caserta
Villa di Briano
Marcianise
Teverola
Maddaloni
Arienzo
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Be
Count
mg/kg
0
5
10
15
20
25
30
35
0
2
4
6
8
10


Be
Percent (%)
mg/kg
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
2
4
6
8
10

5b.5 Calcium (Ca)

Calcium is the fifth element and the third most abundant metal in the earth's crust. The metal is trimorphic and is less chemically reactive than alkaline metals and than the other alkaline-earth metals. It can't be found alone in nature, it's mainly found as limestone, gypsum and fluorite. Seawater contains about 0.15% of calcium chloride.

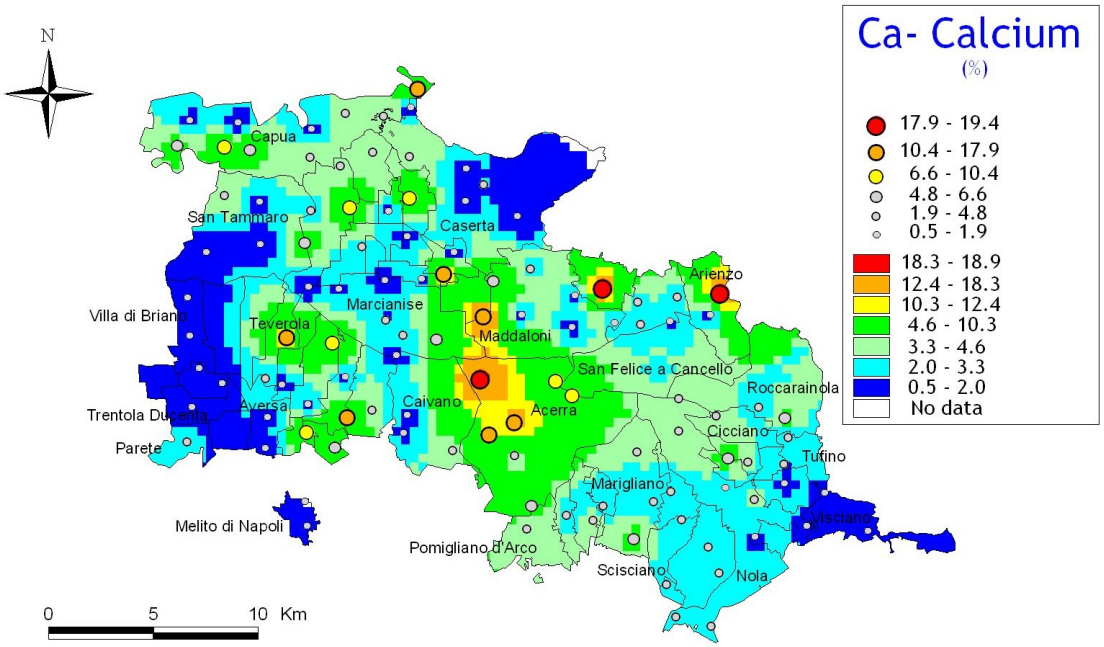
The distribution of calcium is very wide; it is an essential element for the life of plants and animals. Calcium is always contained in every plant, and in the soft tissue, in fluids within the tissue and in the structure of every animal's skeleton. The vertebrate's bones contain calcium in the form of calcium fluoride, calcium carbonate and calcium phosphate.

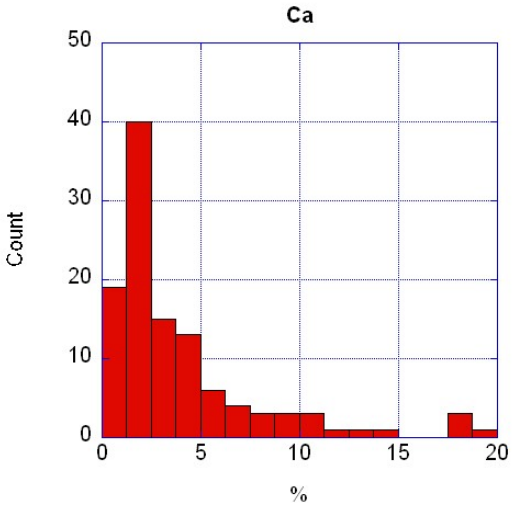
Calcium is the most abundant metal in the human body: is the main constituent of bones and teeth and it has keys metabolic functions. It is most commonly found in milk and milk products, but also in vegetables, nuts and beans. It also assists the functions of nerves and muscles. A high lack of calcium in humans, is one of the main causes of osteoporosis.

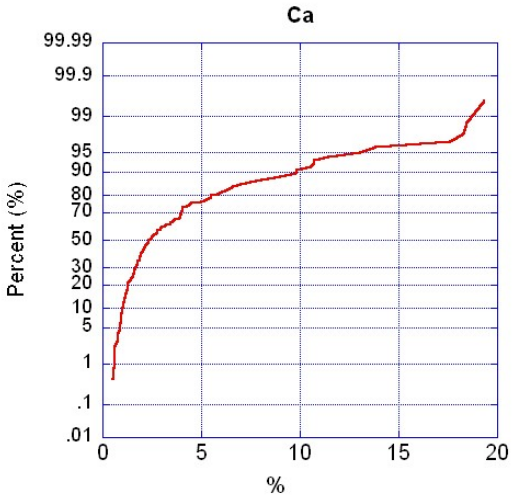
5b.5.1 Distribution of Ca concentrations

Calcium concentrations in soils go from 0.5% to 19.4%. Looking at the interpolated and dot map, areas characterized by low (2.0-4.6 %) and very low (0.5-2.0%) Ca contents are located almost throughout all the Agro Aversano and are interrupted by areas with higher concentrations only in few points. Values over 10.4% occur in Teverola, Succivo, in an area that covers most of the Acerra municipality and part of the Maddaloni and San Marco Evangelista ones, and in an area between Caserta and Capua, along the Volturno river. The highest Ca concentrations (17.9%-19.4%) have been registered in northern Acerra, in Arienzo and in Cervino. In these last two sites, high calcium concentrations have a strong and clear correlation with the dominant carbonatic lithology found going eastward from the Agro Aversano toward Benevento town and the surrounding Sannio area.

Up to 87 of the 113 sampled soils have Ca contents lower than 5.0%, and among these, 59 are even lower than 2.5%. The high presence of relatively low Ca concentrations can be related to the nature of the bedrock lithologies of the Agro Aversano that, especially in its western and southern sectors, have an alluvial and a volcanic origin.


N
Ca- Calcium
(%)
17.9 - 19.4
10.4 - 17.9
6.6 - 10.4
4.8 - 6.6
1.9 - 4.8
0.5 - 1.9
18.3 - 18.9
12.4 - 18.3
10.3 - 12.4
4.6 - 10.3
3.3 - 4.6
2.0 - 3.3
0.5 - 2.0
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Maddaloni
Teverola
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Ca
Count
50
40
30
20
10
0
0
5
10
15
20
%


Ca
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
5
10
15
20
%

5b.6 Cadmium (Cd)

Cadmium is a metal with physical and chemical properties similar to those of zinc.

A large amount of produced cadmium is used in Ni-Cd batteries, the remaining is mainly used for pigments, coatings and plating, and as stabilizers for plastics.

Most of the produced Cd is a by-product of sphalerite (ZnS), in which CdS is present as a significant impurity; for this reason the major Cd mining districts are those associated with zinc; its main producing countries are: Canada, USA, Australia, Mexico, Japan and Peru.

Most of the cadmium found in the environment derives from natural events such as rock's weathering, forest fires and volcanoes. Cadmium is also a by-product of zinc, lead and copper extraction.

Food is the main Cd source for humans; aliments Cd-rich, such as mushrooms, cocoa powder, mussels and shellfish, can increase Cd concentrations in the human organism. People who smoke are particularly exposed to high Cd contents; other high exposures can occur with people who live near hazardous waste sites or factories that release cadmium into the air. Breathing in cadmium can cause lungs damages and also lead to death. Other health effects that can be caused by cadmium are: stomach pains, bone fracture, reproductive failure, possibly DNA damage or cancer development.

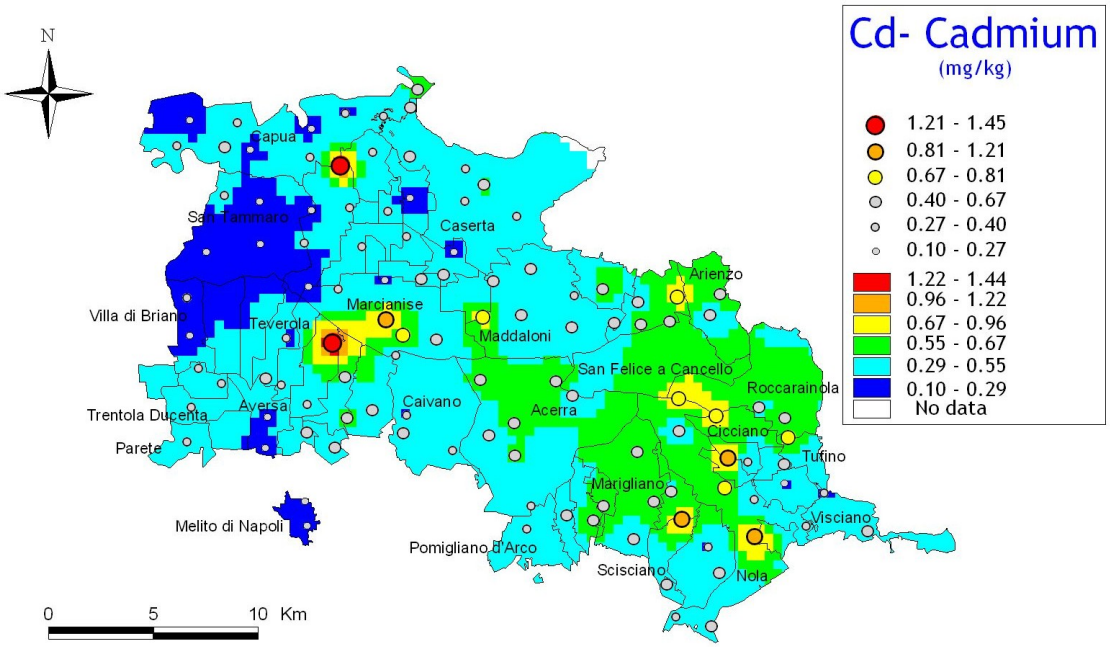
Cadmium may enter in soils and air through industries wastes and combustion of fossil fuels. Artificial phosphate fertilizers are another important Cd source in the environment; the use of such fertilizers increase Cd contents in both soils and waters. Acidified soils promote cadmium uptake by plants and, consequently, Cd absorbed by animals and humans through food increases. Earthworms and other essential soil organisms are very likely to be poisoned by cadmium even at very low concentrations. In aquatic environment Cd can bio-accumulate in mussels, oysters, shrimps, lobsters and fish. Health problems occurred in animals eating or drinking cadmium is the increasing blood-pressure, liver disease and nerve or brain damage.

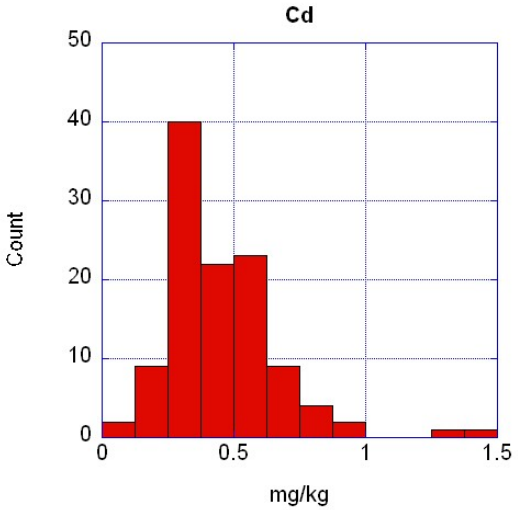
5b.6.1 Distribution of Cd concentrations

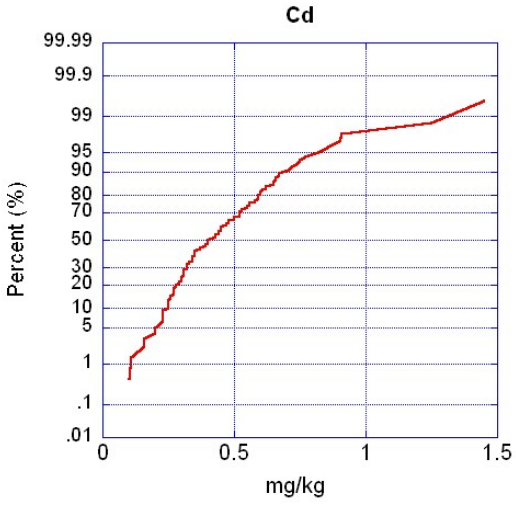
In the soils of the Agro Aversano, cadmium contents range between 0.10 mg/kg and 1.45 mg/kg. Its distribution across the area is quite regular and homogeneous, with values often about 0.10-0.55 mg/kg. Rare exception to this distribution occur in the eastern sector of the Agro Aversano, in which concentrations slightly increase up to 1.22 mg/kg, and in two points in the western sector: one located to the north of Gricignano d'Aversa, and one located to the north of Santa Maria Capua Vetere.

This quite homogeneous distribution for the low concentrations and the presence of two higher samples is well reflected also in the statistical graphs produced.

Cadmium is one of the metals for which Italian legislation has fixed intervention limits. Its limits are at 2 mg/kg for residential areas and at 15 mg/kg for industrial sites; in the sampled area none of these limits is reached.


N
Cd- Cadmium
(mg/kg)
1.21 - 1.45
0.81 - 1.21
0.67 - 0.81
0.40 - 0.67
0.27 - 0.40
0.10 - 0.27
1.22 - 1.44
0.96 - 1.22
0.67 - 0.96
0.55 - 0.67
0.29 - 0.55
0.10 - 0.29
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Cd
Count
50
40
30
20
10
0
0
0.5
1
1.5
mg/kg


Cd
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
0.5
1
1.5
mg/kg

5b.7 Cobalt (Co)

Cobalt is a hard ferromagnetic element with physical properties very similar to those of iron and nickel.

It doesn't occur as a free metal and most of the times is obtained as a by-product of copper and nickel mining activities. The main minerals in which is found are cobaltite, erythrite, glaucodot, and skutterudite. The countries with the major cobalt production: are the Democratic Republic of the Congo, Zambia, China, Australia and Russia.

Cobalt is used in the petroleum and chemical industries, in many alloys, in paints, inks and as Cobalt blue for craftworks and paintings.

Although Cobalt is an essential element for human health (it's a part of vitamin B_{12}), too high concentrations may be harmful. Breathing in high cobalt contents could cause lung problems, such as asthma and pneumonia. This mainly occurs with people that work with cobalt.

Plants grown up on contaminated soils tend to accumulate cobalt in fruits and seeds, thus helping the transmission of cobalt from plants to upper levels of the biological cycle. By the way cobalt is not known to bio magnify up the food chain and, because of this, fruits, vegetables, fish and other animals we eat will usually do not contain very high amounts of cobalt.

Harmful soils are those near mining and melting facilities because they may contain very high amounts of cobalt. In this case the uptake by humans through eating plants can cause serious health problems, such as: heart problems, vomiting and nausea, vision problems and thyroid damage.

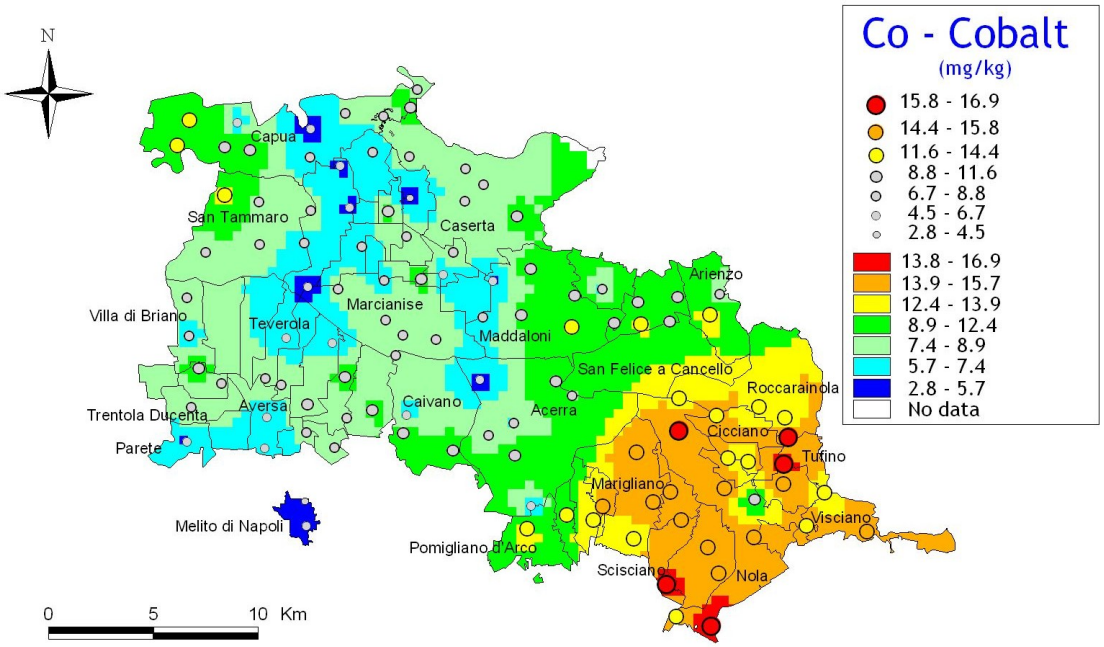
Anthropic contribution to cobalt contents in the environment are mainly related to coal combustion and mining and the production and use of cobalt chemicals.

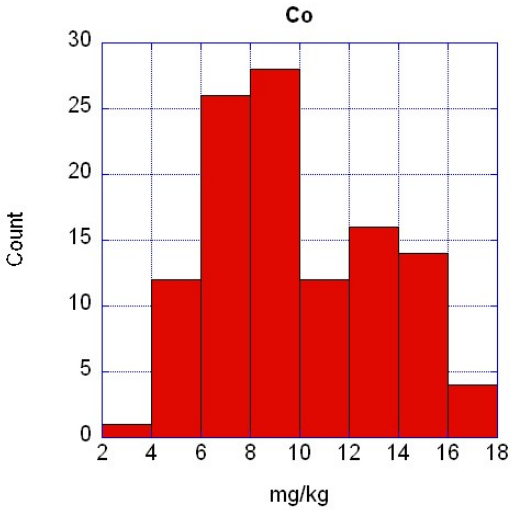
5b.7.1 Distribution of Co concentrations

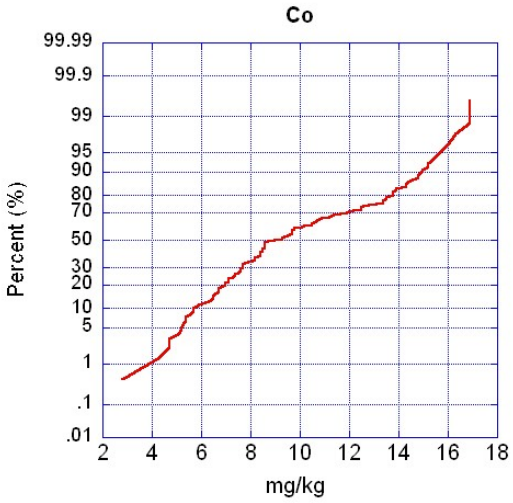
Cobalt contents vary in a range between 2.8 mg/kg and 16.9 mg/kg. The distribution of values follow a regular increasing trend from minimum concentrations (2.8-8.9 mg/kg), found in the north-western sector, to maximum values (14.4-16.9 mg/kg) in the south-easternmost part of the studied area. The highest concentrations (15.8-16.9 mg/kg) occur in two sites sampled near Tufino, in one site to the North of Nola and in two more sites located to the south of Nola and Scisciano. An anomaly of this increasing trend occur to the west of Capua and San Tammaro where values seem to rise (11.6-14.4 mg/kg) in the opposite direction. The distribution of all the high Co contents in the Naples surrounding area, is an evidence of the high influence of the volcanism on the bedrock lithologies and consequently, on the soils developed on them.

From the statistical graphs realized for Co concentrations, is possible to discriminate two main data populations: the first is made up by values varying between 4 mg//kg and 10 mg/kg and includes a large number of samples (66 samples), in the second population values vary from 10 mg/kg to 16 mg/kg and includes about 32 samples. The maximum concentrations are all found in the last interval between 16 mg/kg and 18 mg/kg.

The concentration limits fixed by the Italian Law 152/06 for Co are 20 mg/kg in areas with a residential and recreational use, and 250 mg/kg in industrial areas. In all the analyzed samples Co values never exceed these limit concentrations.


N
Co - Cobalt
(mg/kg)
15.8 - 16.9
14.4 - 15.8
11.6 - 14.4
8.8 - 11.6
6.7 - 8.8
4.5 - 6.7
2.8 - 4.5
13.8 - 16.9
13.9 - 15.7
12.4 - 13.9
8.9 - 12.4
7.4 - 8.9
5.7 - 7.4
2.8 - 5.7
No data
Capua
San Tammaro
Caserta
Villa di Briano
Marcianise
Teverola
Maddaloni
Arienzo
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Sciscian
Nola
0
5
10 Km


Co
Count
mg/kg
0
5
10
15
20
25
30
2
4
6
8
10
12
14
16
18


Co
Percent (%)
mg/kg
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
2
4
6
8
10
12
14
16
18

5b.8 Chromium (Cr)

Chromium naturally occurs with different valences; the two main forms: as Cr (III) and as Cr (VI). The first is an essential nutrient for human health, whose lack may cause diabetes, heart problems and disruptions of metabolism; the last is toxic, particularly harmful for humans and is known to cause many health problems such as lung cancer, breathing problems, ulcers and also death.

Chromium main uses are in alloys, in chrome plating and in metal ceramics. It is also used as dyes and paints, especially in the tanning of leather.

Chromium is mined as chromite ($FeCr_2O_4$) and its major mines are found in South Africa, India, Kazakhstan, Zimbabwe, Finland and Philippines.

Humans can assimilate Cr through skin contact, breathing, drinking and eating, but usually, its levels in air and waters are quite low.

Leather and textile manufacturing is the main anthropic source for both trivalent and hexavalent chromium. Through these activities chromium concentrations in waters rise. Activities such as coal combustion and waste disposal contribute to increase Cr levels in air and soils.

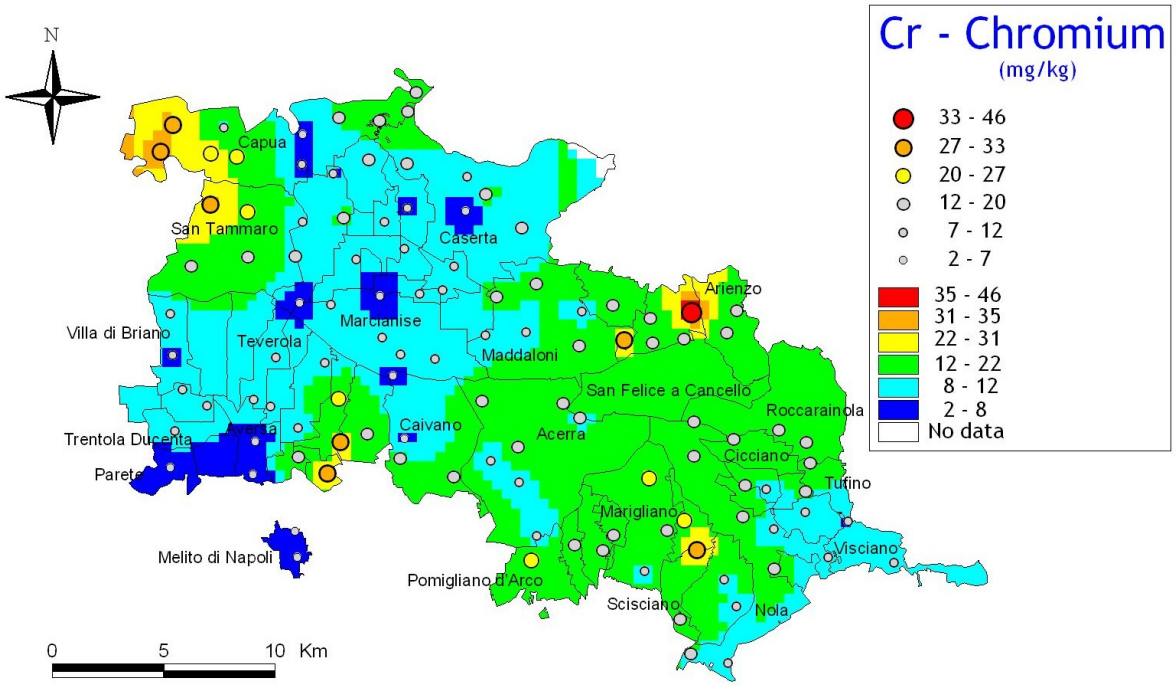
In soils chromium strongly attaches to particles and does not move towards groundwater; in waters it's absorbed on sediments and become immobile. Only a small part of the chromium that ends up in water will eventually dissolve.

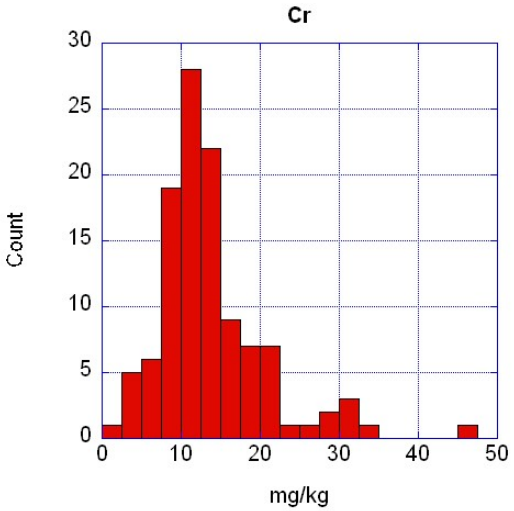
5b.8.1 Distribution of Cr concentrations

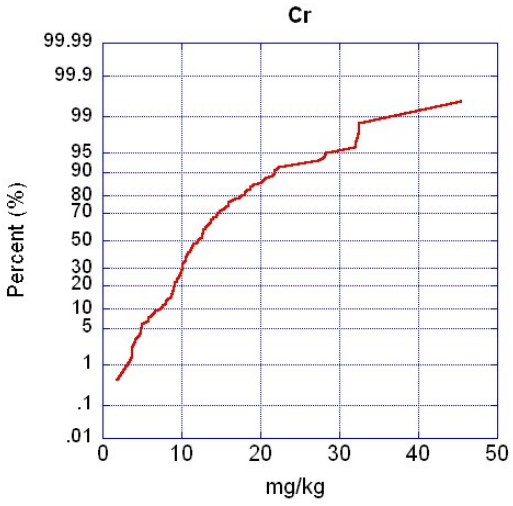
In analyzed soils Cr concentrations range between 2 mg/kg and 46 mg/kg. Low and very low contents (2 mg/kg – 12 mg/kg) are found in a SW-NE orientated area that goes from Parete to Caserta and in a small area between Tufino and southern Nola. High values (27 mg/kg – 33 mg/kg) are not concentrated in one specific area but randomly occur in different locations, in Scisciano, Maddaloni, Sant'Arpino and Succivo. This distribution could be the evidence of local sources of contamination. Other high concentrations are found in the north-westernmost sector of the area, in the municipalities of San Tammaro and Capua and their distribution seem to have a stronger correlation with some geologic features (???). The highest Cr content (46 mg/kg) is in the municipality of Santa Maria a Vico, where could be related to the presence of a great anthropic source of contamination.

The histogram of the Cr distribution show how, most of the analyzed samples (about 104 samples), belong to one population whose range of values is from 2 mg/kg to 22.5 mg/kg. A second population of data is characterized by about 7 samples with concentrations between 22.5 mg/kg to 35 mg/kg. The maximum Cr content registered is an outlier and its value is particularly high respect to those of the intermediate population of data; it can therefore be considered as a clear anomaly.

Concentration limits for Cr total defined by the 152/06 Law are 150 mg/kg and 800 mg/kg respectively for residential and industrial land use; in the investigated area, even where the Cr concentrations are very high, they never exceed the limits fixed by the law.


N
Cr - Chromium
(mg/kg)
33 - 46
27 - 33
20 - 27
12 - 20
7 - 12
2 - 7
35 - 46
31 - 35
22 - 31
12 - 22
8 - 12
2 - 8
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Cr
Count
mg/kg
0
5
10
15
20
25
30
0
10
20
30
40
50


Cr
Percent (%)
mg/kg
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
10
20
30
40
50

5b.9 Copper (Cu)

Copper is a metal with good conductivity of both heat and electricity. Because of this, copper is ideal for the production of electrical wires and other electrical equipment; other fields in which copper is widely used are roofing and plumbing constructions, and the production of alloys such as bronze, brass and cupronickel. It's also used for agricultural purposes.

The main copper ore is represented by chalcopyrite ($CuFeS_2$) whose major mines are found in Chile, USA, Canada, Indonesia and Australia.

Copper can be found into the environment as a result of both natural sources and human activities. Natural sources of copper are forest fires, decaying vegetation and sea spray; anthropic sources are fossil fuel combustion, mining, metal production and phosphate fertilizers production.

Copper is a trace element essential for human health, but prolonged copper exposure by eating, drinking and breathing respectively food, water and air containing very high Cu contents, can cause eminent health problems. The largest harm for human health are copper water-soluble compounds that mainly occur into the environment as result of agricultural practices.

People who live in houses with copper plumbing or near smelters that process copper ore into metal are the ones mainly exposed to high and dangerous Cu concentrations.

The Wilson's Disease is the result of a chronic Cu poisoning; its characteristics are brain damage, renal disease, hepatic cirrhosis and copper deposition in the cornea. Stomachaches, headaches, nose, mouth and eyes irritation are the consequences of prolonged Cu exposure.

In soils copper attaches to organic matter and minerals and can accumulate in plants and animals. High copper contents in soils can cause many problems to the biodiversity of that area because only a limited number of plants have a chance of survival on copper-rich soils. Despite of this, copper-containing manures are still applied on farmlands. Furthermore copper can negatively influence microrganisms and earthworms activities in soils and the organic matter decomposition in these soils can be interrupt.

Animal copper poisoning and related health problems occur in polluted farmlands; sheep are, among all the farm animals, the ones more affected by this kind of poisoning because of their low tolerance to copper.

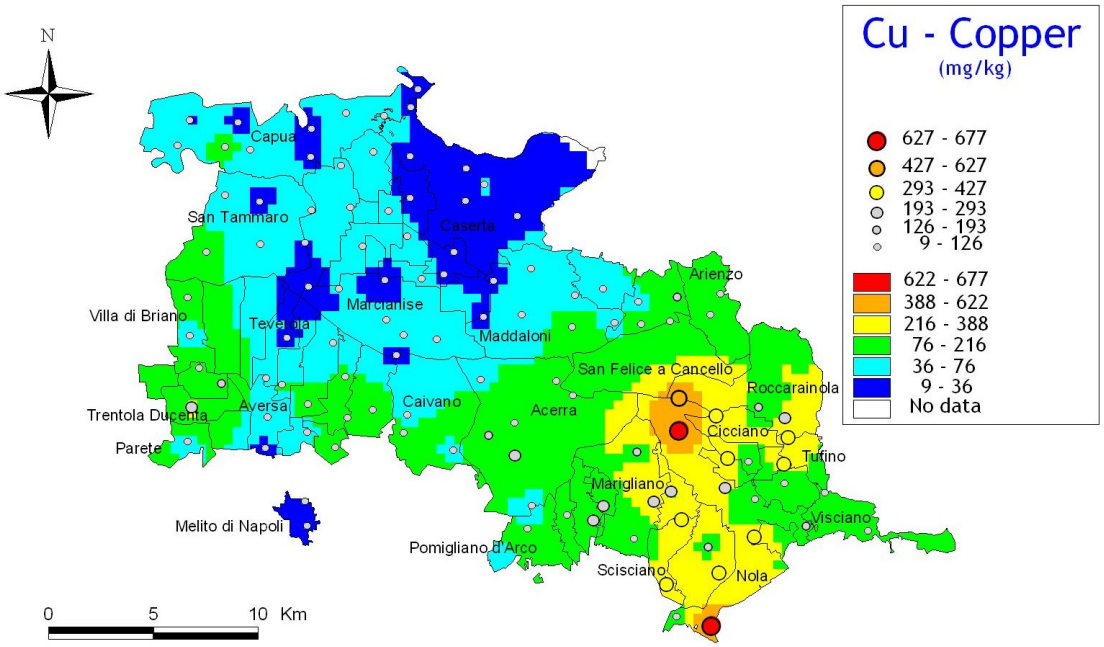
Due to its high stability in soils, copper hardly enters in groundwaters; in surface waters it's mainly transported as sludge particles or as free ions.

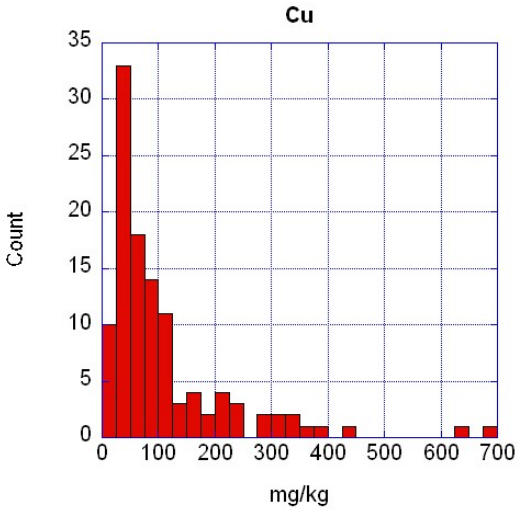
5b.9.1 Distribution of Cu concentrations

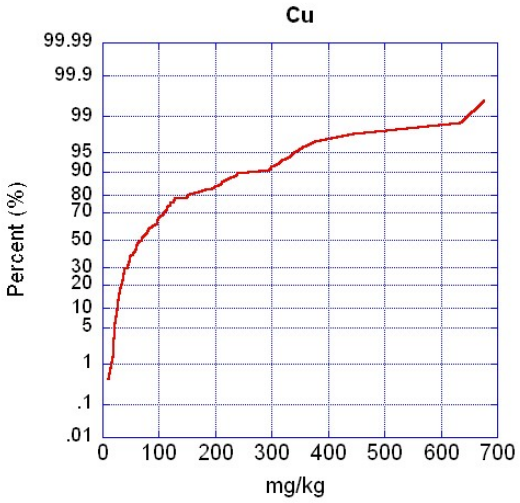
Copper contents registered in the soils of the Agro Aversano range from a minimum value of 9 mg/kg, to a maximum value of 677 mg/kg. Most of the analyzed samples have low and very low Cu concentrations (up to 76 mg/kg) and are mainly located to the north-western part of the area, with a minimum peak of concentration (<36 mg/kg) in Caserta town. Samples with intermediate contents (76 mg /kg – 216 mg/kg) occur in the south-west of the area and in all the eastern sector of it. Values increase in an area comprising Nola, Saviano and most of

the surrounding municipalities such as Cicciano, San Vitaliano, Cimitile and Camposano. The highest values (627 mg/kg - 677 mg/kg) occur in two different sampling sites both located in Nola but one to the north and one to the south of it.

The statistical distribution of Cu values shows how, most of the samples, have concentrations below 125 mg/kg belonging to one single population of data. These sites are also the only ones in which the concentration limit of 120 mg/kg fixed by the 152/06 Environmental Law, for areas with recreational and residential use, is not exceeded. The limit for industrial and commercial areas is 600 mg/kg and, in the two sites with the maximum Cu contents, this limit is reached too.


N
Cu - Copper
(mg/kg)
627 - 677
427 - 627
293 - 427
193 - 293
126 - 193
9 - 126
622 - 677
388 - 622
216 - 388
76 - 216
36 - 76
9 - 36
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Cu
Count
35
30
25
20
15
10
5
0
0
100
200
300
400
500
600
700
mg/kg


Cu
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
100
200
300
400
500
600
700
mg/kg

5b.10 Iron (Fe)

Iron is a silver-gray metal forming two major series of chemical compounds: the ferrous (bivalent iron (II)) and the ferric compounds (trivalent iron (III)).

Due to its low cost and high strength, it's the most used of all the metals. It's widely diffused in many fields of application: from food containers to electrical equipment, from cargo ships to paper staples. Steel is the best known iron alloy.

Iron is one of the, both cosmic and terrestrial, most diffused elements. It is mainly found as iron oxides, and its major minerals are hematite, magnetite, and taconite. The main economic iron mines are in Brazil, China, Russia, Australia, USA, Canada, Venezuela, Sweden and India.

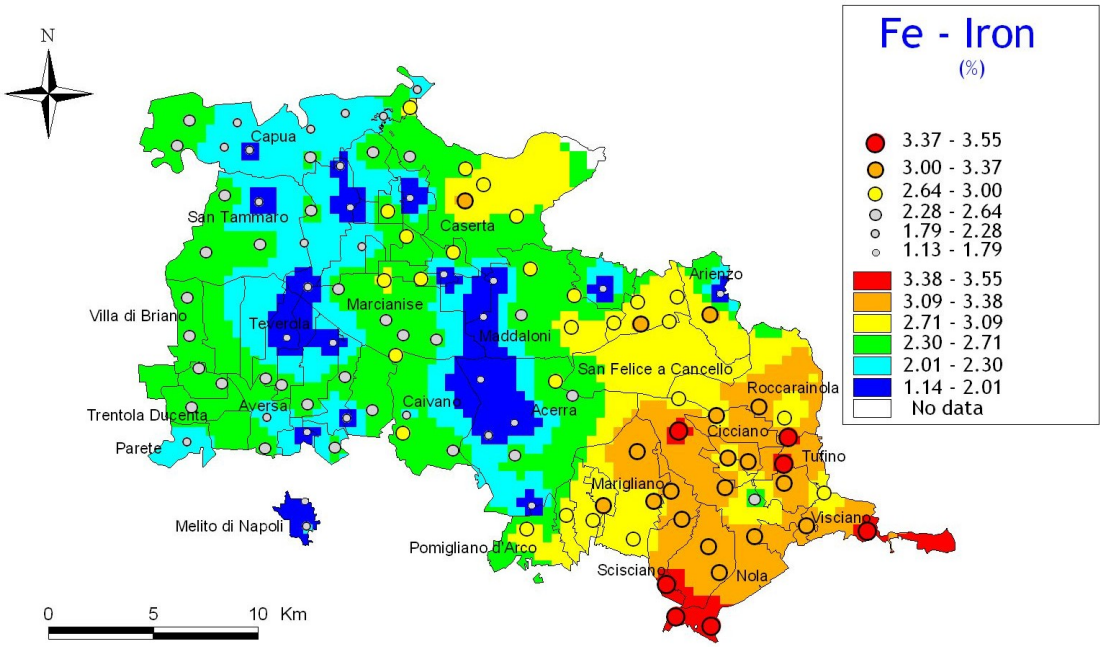
Iron is an essential element for life; it's part of the hemoglobin and a very common problem for human health is iron deficiency and consequent anaemia. The recommended iron daily intake for humans vary between 7 mg for a man to 11 mg for a woman. These contents can be taken through meat, whole meal products, potatoes and vegetables, but iron absorption by human body is faster for iron contained in animal tissues than for iron contained in plants.

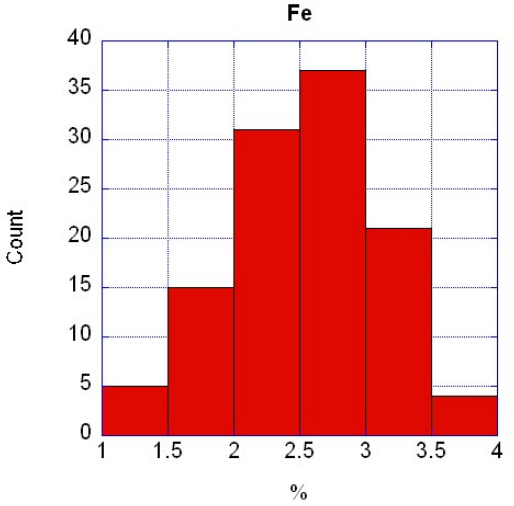
Siderosis and lung cancer are some of the health effects on humans of an excessive iron inhalation; iron can be absorbed by tissues for contacts too and cause conjunctivitis, choroiditis, and retinitis.

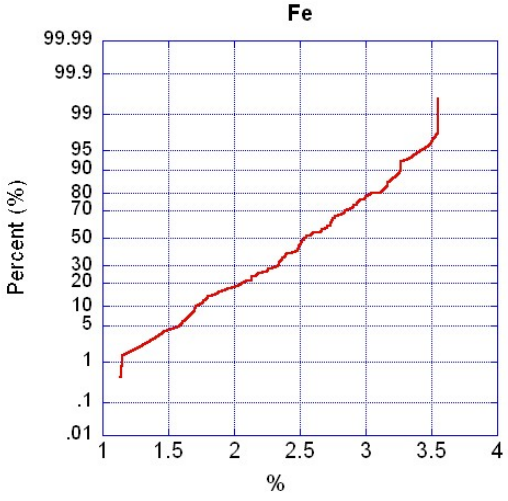
5b.10.1 Distribution of Fe concentrations

Iron concentrations vary between 1.13% and 3.55%. Its distribution pattern shows a quite clear trend with values increasing in correspondence of the volcanic related terrains in the southern part of the studied area; highest values (3.37% - 3.35%) are registered in three sampling sites in the south of Nola and Scisciano, but also in Visciano, Tufino and to the north of Nola. The areas surrounding these high concentrations have all values between 3% and 3.37%, thus showing the presence of a geochemical trend. In this range of values is also found one sample collected in Caserta town. Particularly low Cu contents (1.4% - 2.3%) are found in Melito di Napoli, Capua, San Tammaro, Maddaloni, Acerra and most of the western sector of the investigated area.

The fact that Fe distribution throughout the area follow a regular increasing trend is shown by the statistical graphs realized I which is clear a Gaussian distribution of concentrations.


N
Fe - Iron
(%)
3.37 - 3.55
3.00 - 3.37
2.64 - 3.00
2.28 - 2.64
1.79 - 2.28
1.13 - 1.79
3.38 - 3.55
3.09 - 3.38
2.71 - 3.09
2.30 - 2.71
2.01 - 2.30
1.14 - 2.01
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Sciscian
Nola
0
5
10 Km


Fe
Count
40
35
30
25
20
15
10
5
0
1
1.5
2
2.5
3
3.5
4
%


Fe
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
1
1.5
2
2.5
3
3.5
4
%

5b.11 Mercury (Hg)

Mercury is also known as quicksilver and is a heavy, liquid metal. Its alloys with metals, such as gold, silver, and tin are called amalgams.

Mercury is a metal with a high density and a high rate of thermal expansion; due to these characteristics it's widely used in the production of manometers, barometers and thermometers. Mercury is also widely used in the chemical separation of gold from its ore, thanks to its ease in amalgamating with it. Mercury compounds have many uses: from medicine to insecticides, from disinfectants to rat poisons.

The main mercury ore is cinnabar (HgS); the main production countries are Spain, Russia, Italy, China and Slovenia.

Mercury is naturally present into the environment as a result of weathering of minerals in soils and rocks. Anthropogenic Hg is mainly released into air, through fossil fuel combustion, mining, smelting and solid waste combustion. Mercury release in soils and waters can be caused by industrial wastewater disposal or by the use of agricultural fertilizers.

Mercury found in foodstuff has not a natural origin: it's the result of bio-absorption and bioaccumulation through the food chain. The organisms that absorb the greatest amount of Hg from surface waters are fishes. The Hg compound they absorb is the methyl mercury which forms in acidic surface waters. Humans can also uptake mercury from vegetables and other crops on which sprays containing mercury have been applied.

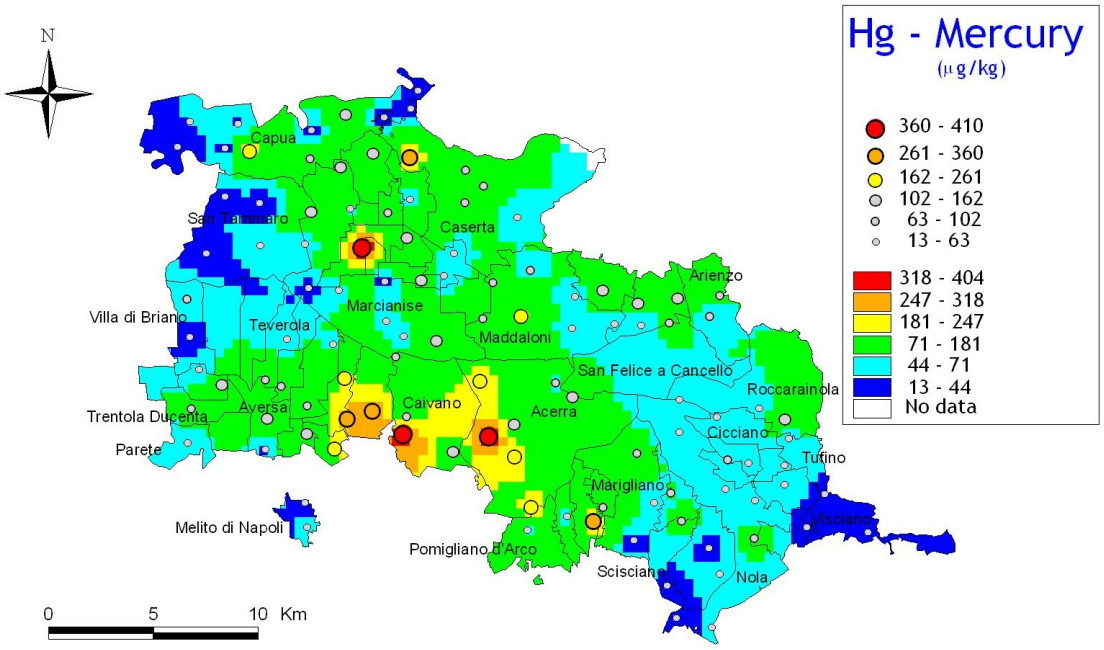
Mercury vapors can be the cause of many health problems, such as nerve, brain and kidney damage, lung irritation, eye irritation and vomiting. Other damages caused by Hg are DNA and chromosomal alteration and reproduction problems such as birth defects and miscarriages.

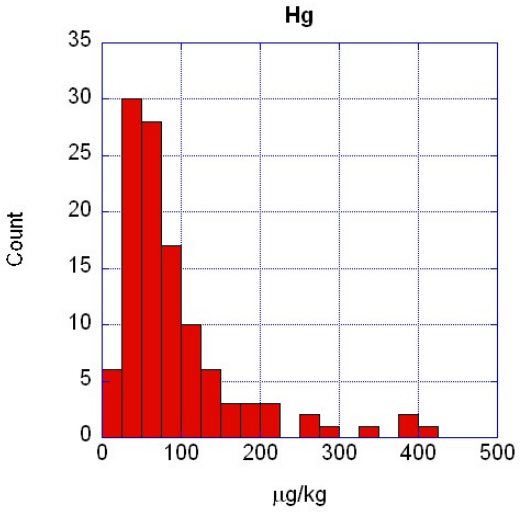
5b.11.1 Distribution of Hg concentrations

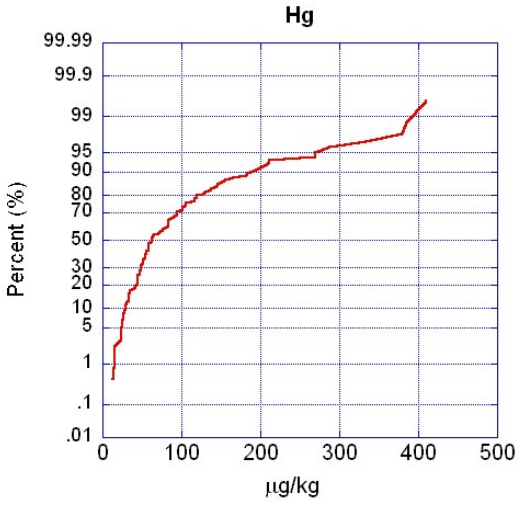
Mercury concentrations range from 13 μg/kg to 410 μg/kg. Its distribution pattern in soils doesn't seem to follow any particular geographic trend. Lowest values (13 μg/kg - 44 μg/kg) are found in Visciano, San Tammaro, Capua and Melito di Napoli; all the surrounding areas have Hg concentrations up to 71 μg/kg. Intermediate values (71 μg/kg – 181 μg/kg) occur in the middle part of the Agro Aversano and the highest Hg contents (360 μg/kg – 410 μg/kg) are in Acerra, Caivano and Macerata Campania. Near Caivano, in the municipality of Orta d'Atella, relatively high Hg concentrations (261 μg/kg – 360 μg/kg) are found, thus suggesting the presence of a diffused contamination source in the area. Other samples with high Hg values are also found to the north of Caserta and in Brusciano.

The histogram and the cumulative frequency curve reveal the presence of a main population of data, whose values are up to 150 μg/kg, and other samples with not regularly distributed concentrations.

Mercury concentration limits in soils have been fixed by law at 1 mg/kg for residential areas, and at 5 mg/kg for industrial and commercial areas. According to these limits, none of the analyzed samples has values exceeding the prescript concentrations.


N
Hg - Mercury
(µg/kg)
360 - 410
261 - 360
162 - 261
102 - 162
63 - 102
13 - 63
318 - 404
247 - 318
181 - 247
71 - 181
44 - 71
13 - 44
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Aversa
Caivano
Acerra
Trentola Ducenta
Parete
Cicciano
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Hg
Count
35
30
25
20
15
10
5
0
0
100
200
300
400
500
µg/kg


Hg
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
100
200
300
400
500
µg/kg

5b.12 Potassium (K)

Potassium is one of the metals belonging to the alkali group.

Almost 95% of all the potassium is used in agricultural fertilizers; the remaining part is used, as compounds, for glass manufacture, liquid soaps and detergents. A little potassium salts is used in pharmaceuticals, medical drips, in baking, photography and tanning leather.

The major potassium minerals mined are pinkish and sylvite, carnallite and alunite; the main mining countries are Canada, USA and Chile.

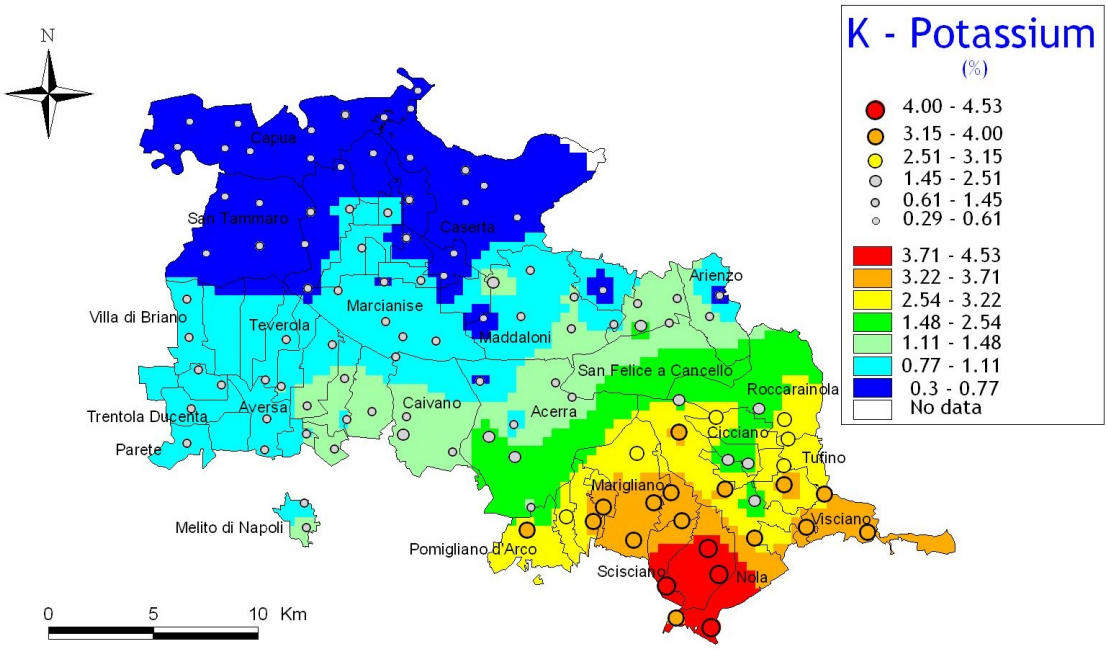
Potassium is mainly found into the environment, and especially in the sea (0.75 g/l), as result of weathering processes on K-rich minerals such as feldspars and clays.

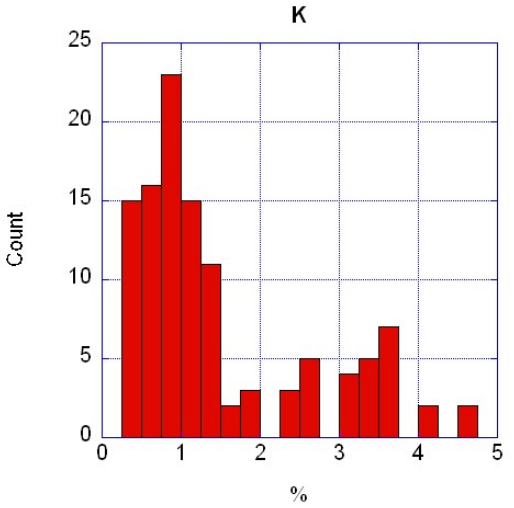
In the human body, potassium assists nerve function; it can be taken into the organism through bread, vegetables, nuts, meat, fruit, milk and potatoes. Potassium inhalation can cause irritation of the eyes, nose, throat and lungs; higher exposures may cause an increase of fluid in the lungs, and even lead to death.

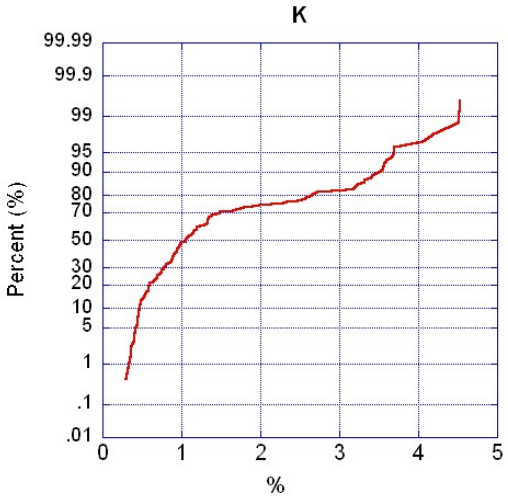
Potassium influences plants photosynthesis and is, therefore, one of the essential elements for plants survival, along with nitrogen and phosphorous. Its presence into the environment is fundamental for plant growth, soil health and animal nutrition.

5b.12.1 Distribution of K concentrations

Potassium contents in the soils of the Agro Aversano vary from a minimum of 0.29% to a maximum of 4.53%. Its distribution pattern is clearly influenced by the presence of the volcanic rocks belonging to the Neapolitan Volcanic Province, mainly characterized by potassic and ultra-potassic products. Values regularly increase from north-west (0.3% - 0.77%) to south-east; highest contents (4% - 4.54%) are registered to the south of Nola, Saviano and Scisciano. The presence of these positive anomalies is also shown in the histogram of K concentrations, where a family of data with low values is clearly separated by other sub-families with higher values.


N
K - Potassium
(%)
4.00 - 4.53
3.15 - 4.00
2.51 - 3.15
1.45 - 2.51
0.61 - 1.45
0.29 - 0.61
3.71 - 4.53
3.22 - 3.71
2.54 - 3.22
1.48 - 2.54
1.11 - 1.48
0.77 - 1.11
0.3 - 0.77
No data
Capua
San Tammaro
Caserta
Arienzo
Marcianise
Villa di Briano
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


K
Count
25
20
15
10
5
0
0
1
2
3
4
5
%


K
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
1
2
3
4
5
%

5b.13 Magnesium (Mg)

Magnesium is a metallic element that constitutes about 2% of the Earth's crust by weight; in seawaters, it is the third most abundant dissolved element.

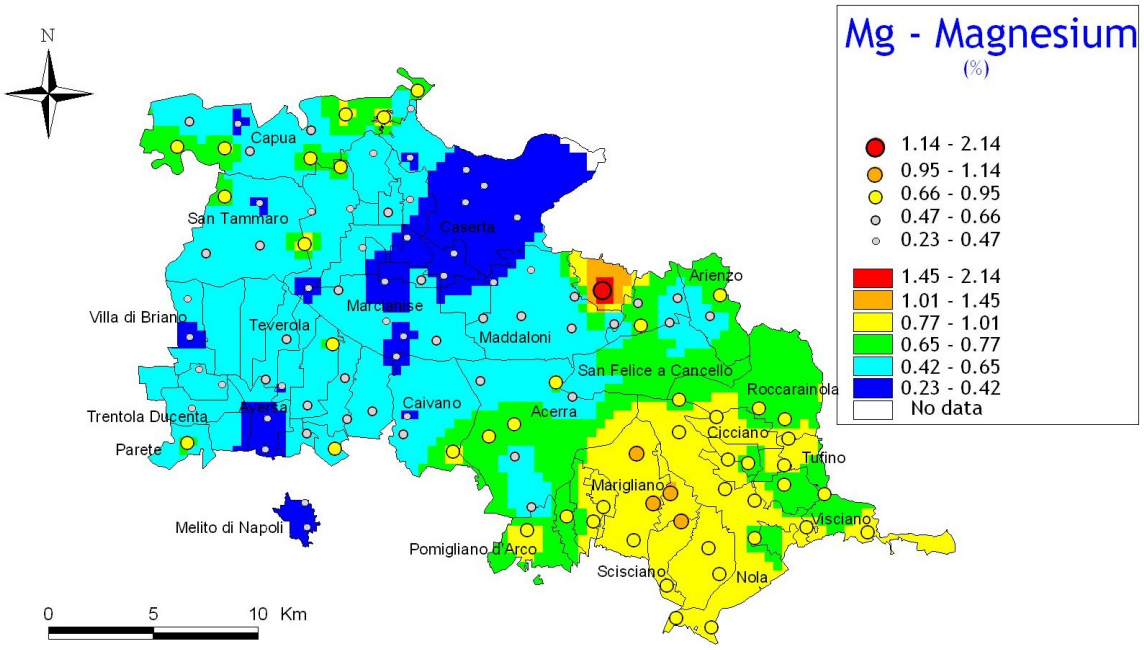
Magnesium and its compounds are used as refractory material, as removal of sulphur form iron and steel, in airplane and missile construction, in flashlights, in pyrotechnics and in agriculture.

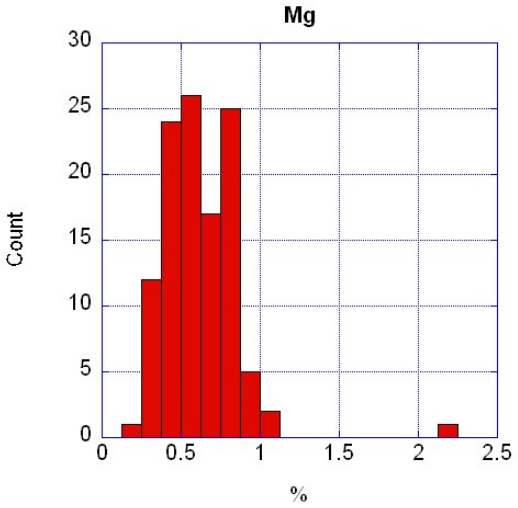
In nature it's found in many minerals, the most common are dolomite, magnesite, olivine and serpentine. The major production countries of this metal are: USA, China, Russia, Turkey, North Korea, Slovakia, and Greece.

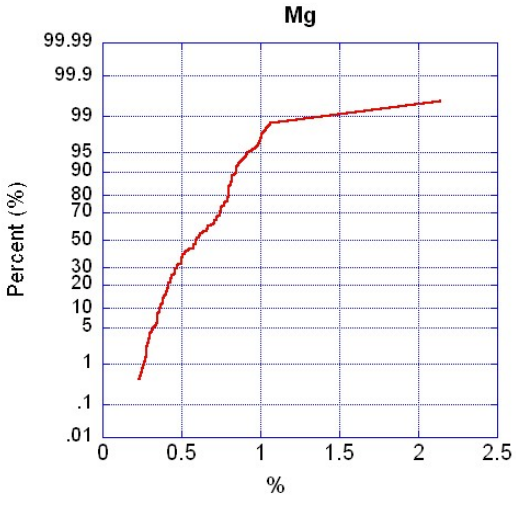
Humans need an average daily Mg intake of about 200 mg. It is an element considered to have low toxicity and not to be harmful for human health. It can enter in the body by inhalation, ingestion or by skin contact but it doesn't cause serious damages.

5b.13.1 Distribution of Mg concentrations

Magnesium concentrations in the Agro Aversano vary in a range between 0.23% and 2.14%. Looking at the geochemical map realized on the basis of Mg contents in soils, there are some differences between the eastern and the western sector of the studied area. Minimum contents (0.23% - 0.42%) are mostly found in Aversa, Melito di Napoli, in Caserta town and in part of the surrounding municipalities. Low values (0.42% - 0.65%) characterize all the western sector of the Agro Aversano, while high and relatively high contents (0.65% - 1.45%) characterize most of the eastern sector. The highest Mg contents (2.14%) is registered in Cervino and, as shown by the related histogram, is an isolated anomalous value that can be probably related to a local source of pollution.


N
Mg - Magnesium
(%)
1.14 - 2.14
0.95 - 1.14
0.66 - 0.95
0.47 - 0.66
0.23 - 0.47
1.45 - 2.14
1.01 - 1.45
0.77 - 1.01
0.65 - 0.77
0.42 - 0.65
0.23 - 0.42
No data
Capua
San Tammaro
Caserta
Arienzo
Marcianise
Villa di Briano
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Mg
Count
30
25
20
15
10
5
0
0
0.5
1
1.5
2
2.5
%


Mg
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
0.5
1
1.5
2
2.5
%

5b.14 Manganese (Mn)

Manganese is a hard metal that hardly melt, but easily oxidized.

It is essential to iron and steel production and is a key component of low-cost stainless steel and some aluminum alloys. Its most diffused compounds are potassium permanganate and manganese oxide; the first is a potent oxidizer and is used as a disinfectant, the last is used into fertilizers and ceramics.

Manganese usually occurs in soils as oxides and hydroxides, such as pyrolusite (MnO_2) and rhodochrosite ($MnCO_3$). The main mining areas for manganese are Australia, Russia, Gabon Ukraine, Georgia, and South Africa.

Human deriving Mn is released in the air by industrial activities and through fossil fuels burning; it can pass into surface water and groundwater and enter in soils through manganese pesticides use.

Manganese is a toxic essential trace elements, which means that humans do need it to survive, but not over a certain amount. Too low Mn contents in human body can cause health problems, but too high concentrations can be toxic.

Humans can uptake Mn through food, such as spinach, tea and herbs, the highest Mn concentrations in food are in grains and rice, soya beans, eggs, nuts, olive oil, green beans and oysters.

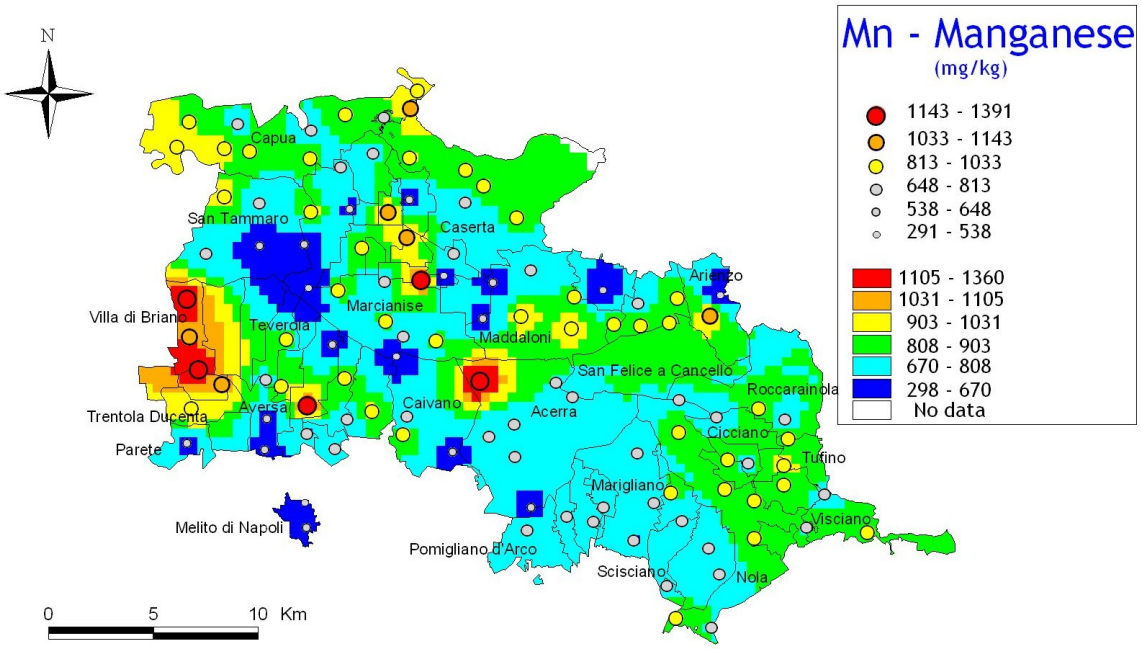
A long-term inhalation of Mn dust and fume can lead to manganese poisoning, whose main effects are hallucinations, forgetfulness and nerve damage. Other health effects caused by manganese are Parkinson disease, lung embolism, bronchitis and, in men subjected to prolonged Mn exposure, impotence.

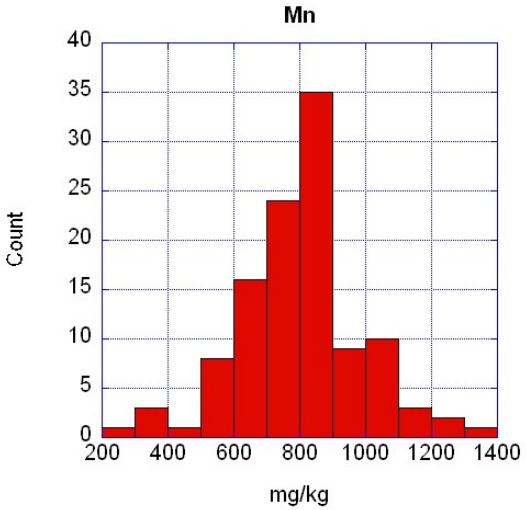
From soils Mn is absorbed by the plants who transport manganese ions to the leaves. As for human beings, so for plants, manganese can cause both toxicity and deficiency symptoms. Manganese deficiency are more common in acid soils.

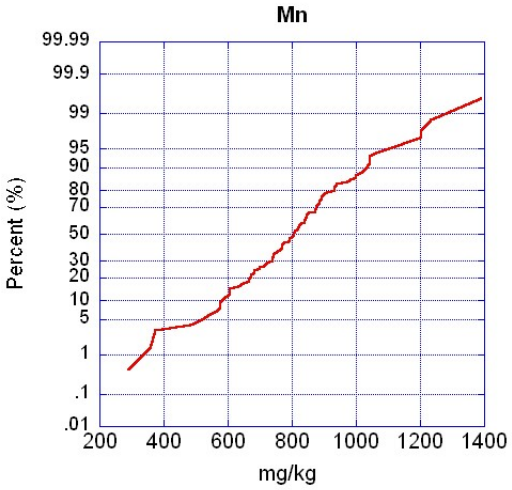
5b.14.1 Distribution of Mn concentrations

The concentrations of Mn range from 291 mg/kg to 1391 mg/kg. The distribution of its contents throughout the Agro Aversano doesn't have any particular pattern, both low and high values are randomly distributed. The maximum Mn concentrations (1143 mg/kg – 1391 mg/kg) are found in north-western Acerra, in Capodrise, in Gricignano d'Aversa and in Villa di Briano. In the latter municipality, all the collected samples, registered high and very high Mn values, which can be probably related to an extended source of contamination.

In the statistical graphs realized with Mn contents, is possible to discriminate a main population of data, whose values regularly increase from 500 mg/kg to 900 mg/kg, with a peak of 35 samples in the interval between 800 mg/kg and 900 mg/kg. A smaller population ranges between 200 mg/kg and 500 mg/kg.


N
Mn - Manganese
(mg/kg)
1143 - 1391
1033 - 1143
813 - 1033
648 - 813
538 - 648
291 - 538
1105 - 1360
1031 - 1105
903 - 1031
808 - 903
670 - 808
298 - 670
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Mn
Count
mg/kg
0
5
10
15
20
25
30
35
40
200
400
600
800
1000
1200
1400


Mn
Percent (%)
mg/kg
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
200
400
600
800
1000
1200
1400

5b.15 Sodium (Na)

Sodium is a soft alkaline metal with a low melting point.

Sodium is used in the production of some alloys, in soap, in sodium vapor lamps and to make glass.

It is, after chlorine, the most abundant element dissolved in seawaters. The sodium compounds commonly occurring into the environment are: sodium chloride (NaCl), also known as halite or rock salt, sodium borate, known as borax, sodium carbonate, known as soda or trona, sodium sulphate and sodium nitrate. These salts occur in seawater (1.05%), salty lakes, alkaline lakes and mineral spring water.

Sodium salts production is around 200 million ton/year; it is mainly extracted by pumping up brine from salt deposits through pumping water down bore holes to dissolve it.

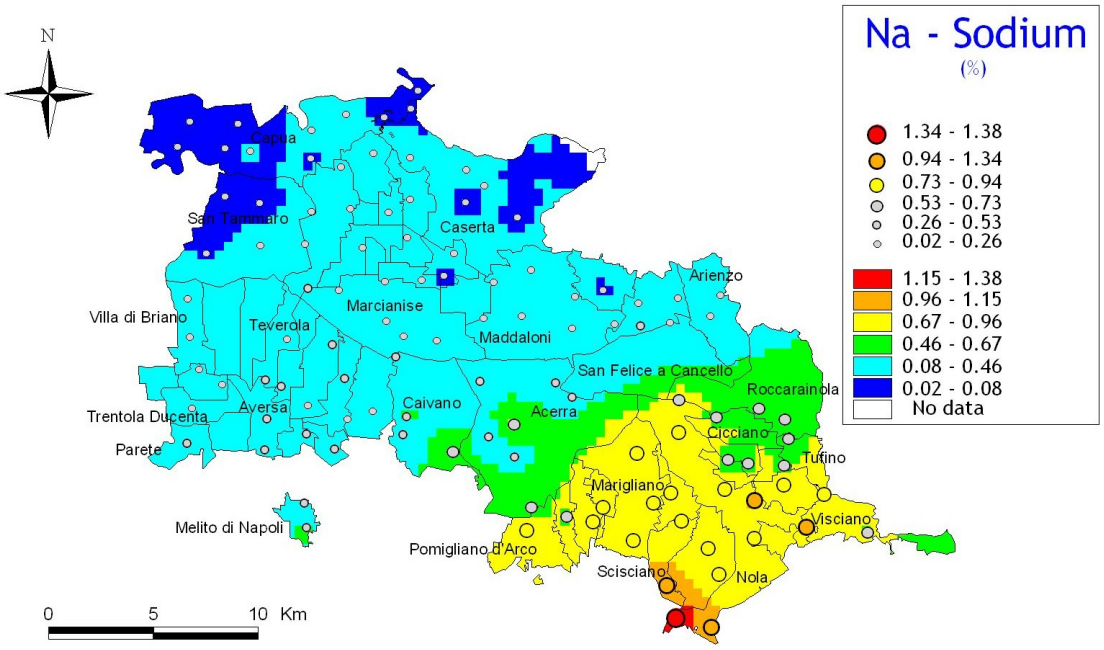
Sodium is found in many foodstuffs, it is required for nerve and muscle functioning. Too high sodium amount can cause problems to kidneys and increases the chances of high blood pressure.

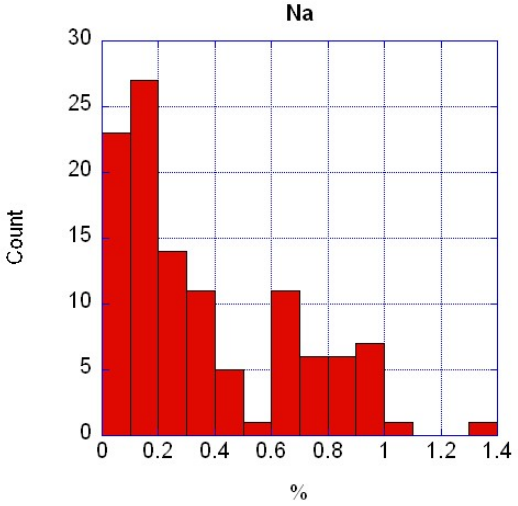
Sodium hydroxide fumes form when Na combines with water; they are highly irritating for skin, throat, nose and eyes.

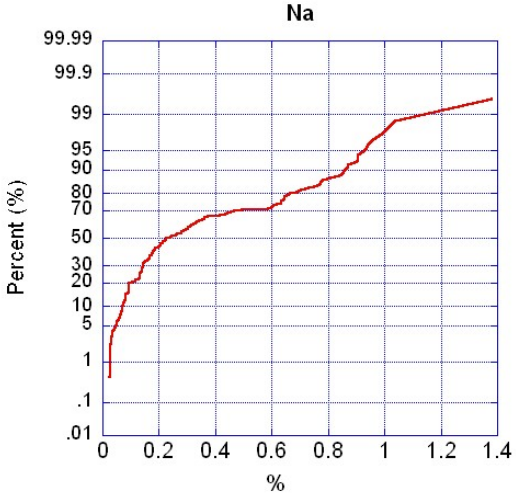
5b.15.1 Distribution of Na concentrations

Sodium contents in soils range from 0.02% and 1.38%. Most of the area is identified by low and very low values varying between 0.02% and 0.46%; these values occur from the north-western sector, were are values are the lowest, to the municipalities of Acerra and San Felice a Cancello. Here sodium contents start increasing with concentrations up to 0.96% and reach the highest values (0.96%-1.38%) in southern Scisciano and southern Nola. Values follow a regular trend also shown in the cumulative frequency curve and in the histogram realized. Most of the analyzed samples (about 70%) have sodium contents below 0.6%, about 25-29% of the samples have values between 0.6% and 1%, and just two samples have values higher than 1%.

As a member of the first group of the Periodic Table of the elements, sodium concentrations in soils, could be very likely related to the Neapolitan volcanism; an evidence of this, is the regular increasing trend of its values south-eastward.


N
Na - Sodium
(%)
1.34 - 1.38
0.94 - 1.34
0.73 - 0.94
0.53 - 0.73
0.26 - 0.53
0.02 - 0.26
1.15 - 1.38
0.96 - 1.15
0.67 - 0.96
0.46 - 0.67
0.08 - 0.46
0.02 - 0.08
No data
Capua
San Tammaro
Caserta
Arienzo
Marcianise
Villa di Briano
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Aversa
Caivano
Acerra
Trentola Ducenta
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Na
Count
30
25
20
15
10
5
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
%


Na
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
0.2
0.4
0.6
0.8
1
1.2
1.4
%

5b.16 Nickel (Ni)

Nickel is a ductile metal, it is a fairly good conductor of heat and electricity.

It is mainly employed for the production of many ductile, strong, heat and corrosion resistant alloys. Nickel is also used in rechargeable batteries, catalysts, coinage, foundry products, plating and jewelry.

Nickel mostly occurs combined with sulphur and arsenic; it is mainly extracted in iron-nickel sulphides ores and its major mining districts are Russia, Australia, New Caledonia, Cuba, Canada and South Africa.

The average nickel content in soils is around 20 ppm, but it can vary between 0.2 ppm and 450 ppm. Foodstuffs naturally contain small amounts of nickel; its major food sources are beans and tea; also chocolate and fats are known to contain high Ni contents.

Nickel can enter human body through breathing, smoking cigarettes, and drinking or eating food containing high Ni values, but also through skin contact with nickel-contaminated soils or waters.

If assumed in small quantities nickel is an essential element, too high concentrations can be a harm to human health and cause problems such as: skin rashes and allergic reactions, lung embolism, asthma and chronic bronchitis, heart problems and higher chances of cancer development.

Anthropic activities releasing Ni into the air, are power plants and trash incinerators; it is also released in surface water when it's contained in wastewater streams.

For animals small amounts of nickel are an essential nutrient, but uptake in excessive doses can also be dangerous. Nickel doesn't accumulate in plants or animals so it doesn't bio magnify up the food chain.

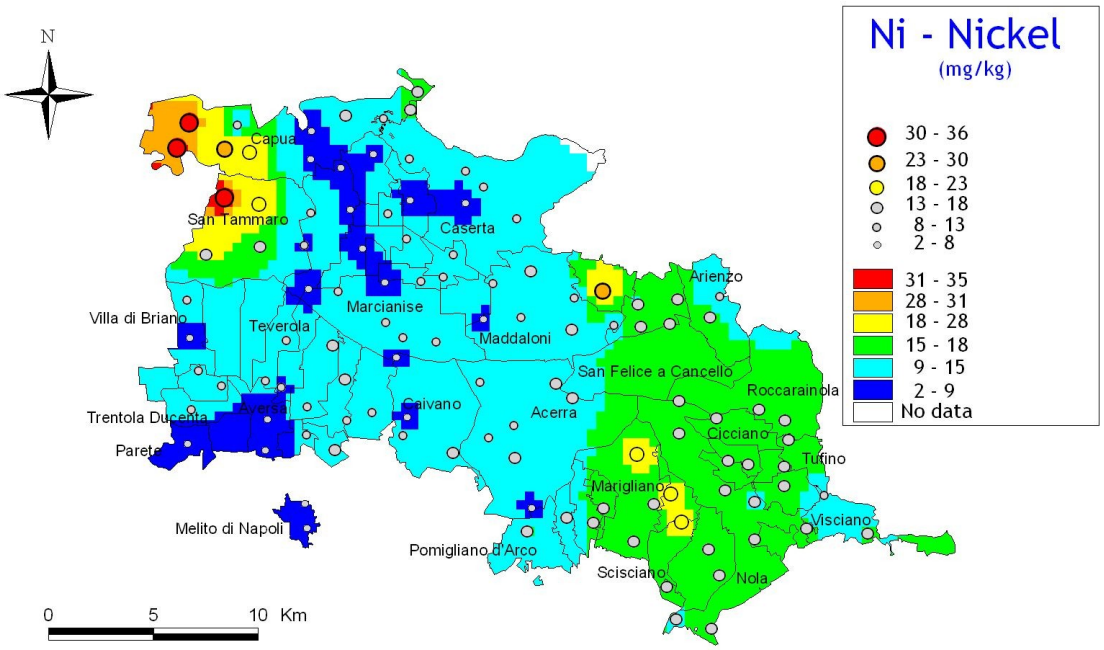
5b.16.1 Distribution of Ni concentrations

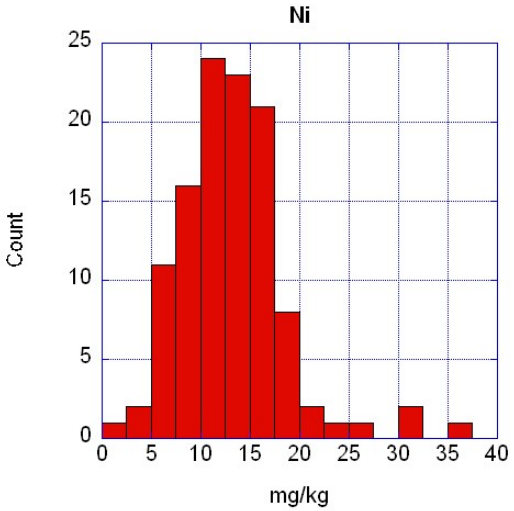
In the soils of the Agro Aversano, nickel contents vary in a range between a minimum value of 2 mg/kg and a maximum value of 36 mg/kg. Low and very low values (2 mg/kg – 15 mg/kg) are all located in the central part of the area, from Caserta to Caivano, extending from Parete, to Pomigliano d'Arco. Moving eastward from Acerra to Visciano, average values are about 15 mg/kg – 18 mg/kg, with four anomalously high points in which values increase up to 28 mg/kg. Among these four sites, three are found in an area around north Marigliano, San Vitaliano and Scisciano, and one, slightly higher, occurs in Cervino. In all the Agro Aversano the highest Ni contents have been registered in three sampling sites all located in the north-westernmost part of the area, in the municipalities of Capua and San Tammaro. Their distribution seems to be representative of a geological local control.

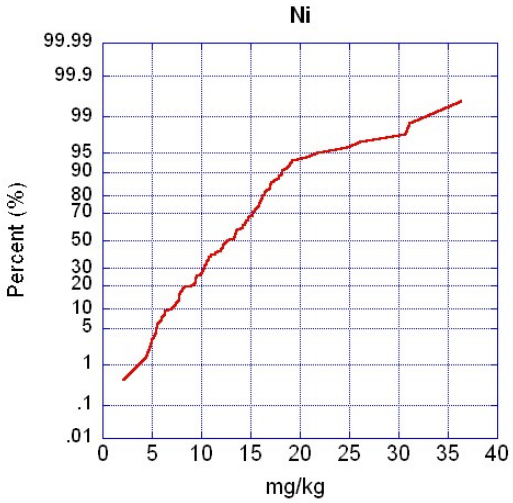
Both histogram and cumulative frequency curve related to nickel concentrations, show that most of the samples (up to 95% of the samples) have values below 20 mg/kg; few of them (4 samples) have Ni concentrations up to 27.5 mg/kg and other four samples have values higher than 30 mg/kg.

Nickel is one of metal whose concentration limits have been fixed by the Italian Environmental Law 152/06: these limits are 120 mg/kg and 500 mg/kg respectively for

residential areas and industrial areas. In none of the analyzed samples Ni contents exceed these intervention limits.


N
Ni - Nickel
(mg/kg)
30 - 36
23 - 30
18 - 23
13 - 18
8 - 13
2 - 8
31 - 35
28 - 31
18 - 28
15 - 18
9 - 15
2 - 9
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Cancello
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Sciscianо
Nola
0
5
10 Km


Ni
Count
mg/kg
0
5
10
15
20
25
30
35
40


Ni
Percent (%)
mg/kg
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
5
10
15
20
25
30
35
40

5b.17 Phosphorous (P)

Phosphorous is a multivalent nonmetal element, essential for the life of many organisms.

It has several forms, known as white, red and black phosphorous. White phosphorous is the one glowing in the dark, is spontaneously flammable when exposed to air and is deadly poison; red phosphorous can vary in color from orange to purple, and black phosphorous looks like graphite, is an electrical conductor and is made under high pressure.

Phosphorous main ore is fluoroapatite; its main mining areas are Russia, USA, Morocco, Tunisia, and Togo. Phosphates concentrations in the oceans are usually very low, due to the insolubility of aluminum and calcium phosphates that, for this reason, accumulate into the deep.

Concentrated phosphoric acids are used in agricultural fertilizers. Phosphates applications are in pyrotechnics, pesticides, in steel production, in military applications (incendiary bombs, smoke screenings etc.).

In the environment P is mainly found as phosphates, that is one P atom bonded to four oxygen atoms (PO_4^{3-}); in natural environment phosphorous is also found as organophosphates in which organic molecules attach to oxygen atoms.

Phosphorous contents in foodstuffs are very high for tuna, salmon, sardines, liver, turkey, chicken, eggs and cheese (200 g/100 g).

Phosphates are important substances for both humans and plants. Phosphate recommended daily intake for humans is about 800 mg/day. Health problems can be caused by both excessive or too low phosphates intake.

White phosphorus is the most harmful phosphorus form for human health; it is extremely poisonous and in many cases exposure to it can be fatal. White phosphorus can cause skin burns and cause damages to the liver, the heart or the kidneys.

In soils white phosphorus is converted into less harmful forms only after several days, but it can be kept in its dangerous form for thousands of years if contained in deep soils and rivers and lakes bottoms.

Phosphates are anthropically released into the environment through to mining and cultivating.

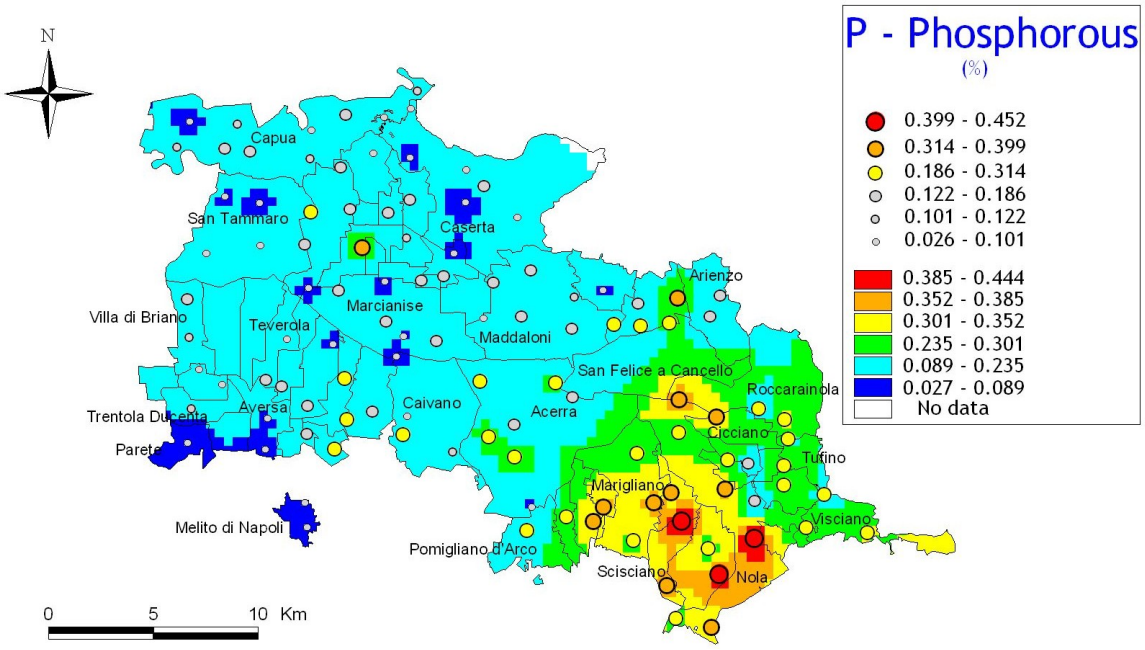
The increasing phosphor concentrations in surface waters causes the phenomenon known as eutrophication, which is related to an increasing growth of phosphate-dependent organisms.

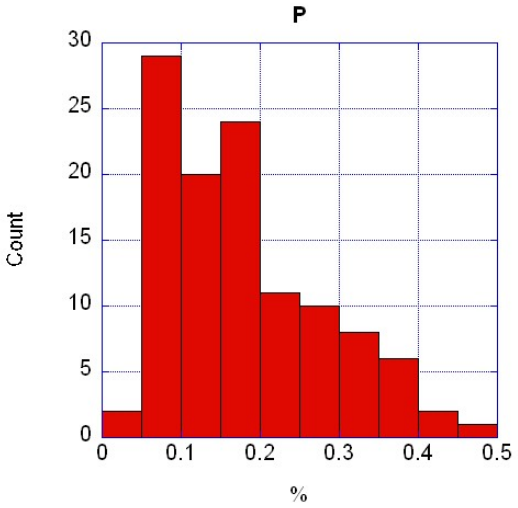
5b.17.1 Distribution of P concentrations

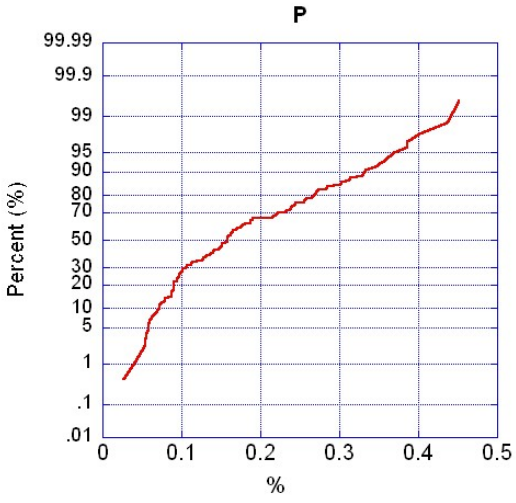
In the analyzed soils of the Agro Aversano phosphorus values vary between 0.027% and 0.452%. Most of the studied area is characterized by low and very low values (0.027%-0.235%); they increase (up to 0.399%) only in the south-eastern sector, near Marigliano and San Felice a Cancello, and have a high positive peak in Nola, Saviano and Scisciano (0.399%-0.452%).

The distribution of phosphorus concentrations is also shown in the statistical graphs realized; about 70% of the total samples (75 samples) have contents up to 0.2%; the rest of the

them gradually increase in values and the highest concentrations (>0.4%) are found in just three samples.


N
P - Phosphorous
(%)
0.399 - 0.452
0.314 - 0.399
0.186 - 0.314
0.122 - 0.186
0.101 - 0.122
0.026 - 0.101
0.385 - 0.444
0.352 - 0.385
0.301 - 0.352
0.235 - 0.301
0.089 - 0.235
0.027 - 0.089
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Aversa
Caivano
Acerra
Trentola Ducenta
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


P
Count
%
0
5
10
15
20
25
30
0
0.1
0.2
0.3
0.4
0.5


P
Percent (%)
%
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
0.1
0.2
0.3
0.4
0.5

5b.18 Lead (Pb)

Lead is a metal element, with a relatively poor electricity conductivity and a high resistance to corrosion. Its isotopes are the end products of each of the three series of naturally occurring radioactive elements.

One of the main applications of Pb is for the production of lead-acid car batteries; it's also used in ceramic glazes, in organ pipes, as electrodes and in computers and televisions screens with the function of radiations shield for viewers.

The main lead mineral is Galena (PbS), it's mined in Australia, USA, China, Peru' and Canada. Some lead is also mined in Mexico and Germany.

Even if lead is a naturally occurring element, most of its environmental concentrations are the result of anthropic activities, especially of leaded gasoline combustion and of industrial emissions and waste disposals.

The lead-cycle created by human activities is much more extended than the natural lead-cycle, this has caused lead pollution to be a worldwide problem.

Lead can be added to human body through contaminated food, water and air; it is one of metals with the most harmful effects on human health. It can cause: disruption of the biosynthesis of hemoglobin and anemia, rise in blood pressure, kidney damage, miscarriages and subtle abortions, brain damage and many others.

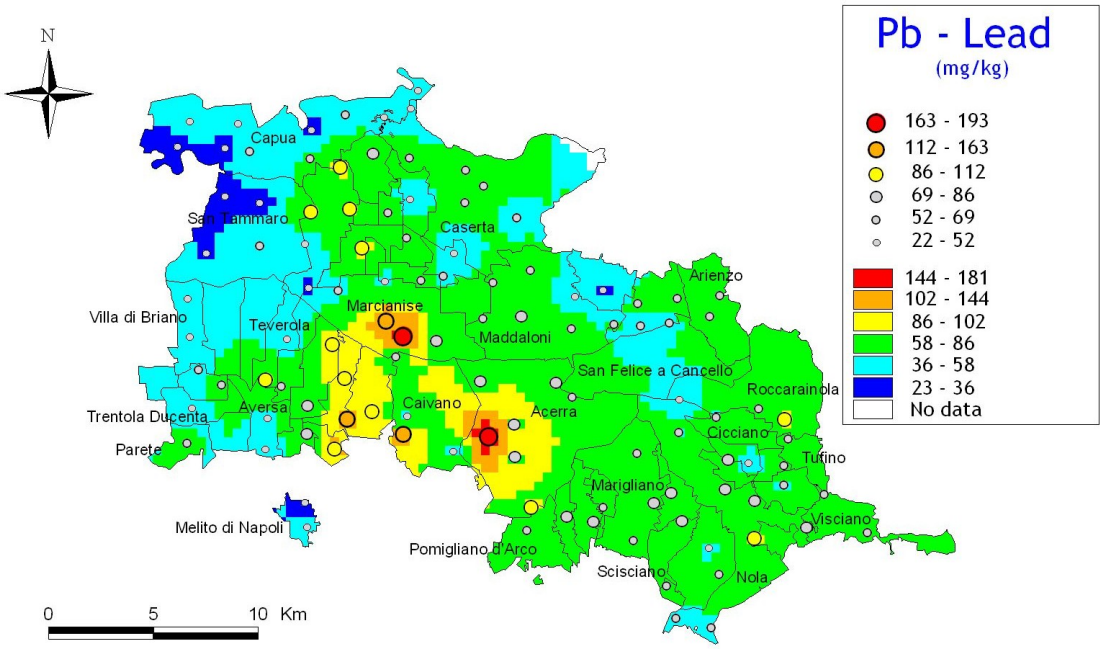
During pregnancy lead can enter into the fetus through mother placenta and can cause serious damages to the nervous system and the brains of unborn children.

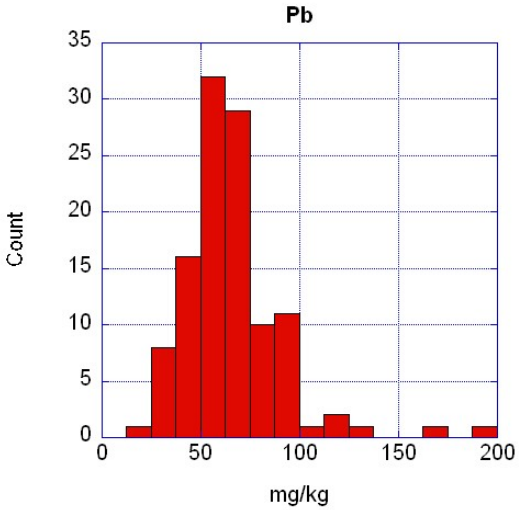
5b.18.1 Distribution of Pb concentrations

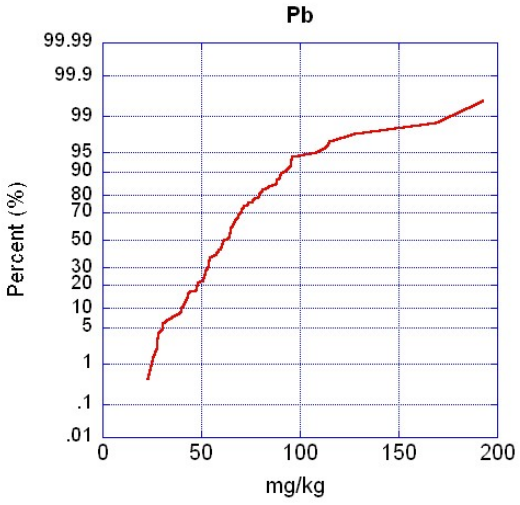
Lead contents in the soils of the Agro Aversano range between 22 mg/kg and 193 mg/kg. Its distribution throughout the area is not regular; lowest values (22 mg/kg – 58 mg/kg) occur only in a restricted area near San Tammaro and Capua, in Marigliano, and in part of the surrounding municipalities. In the rest of the Agro Aversano Pb concentrations are generally around 58 mg/kg and 86 mg/kg, and increase up to the maximum values (163 mg/kg - 193 mg/kg) in the southern-central sector, in the municipalities of Caivano, Succivo and surrounding areas; highest peak of concentrations occur in Marcianise and Acerra.

Looking at the histogram and at the cumulative frequency curve of lead concentrations, is possible to discriminate a main population of data, whose values vary between the minimum of 22 mg/kg, to 100 mg/kg, and another population made up by 6 samples, with values from 100 mg/kg to 193 mg/kg.

According to the 152/06 Environmental Law, Pb content in soils of residential areas should be lower than 100 mg/kg; this concentration limit is not respected in a wide sampled area in the southern central part of the Agro Aversano (Acerra, Caivano and Marcianise territory). In particular values exceed 100 mg/kg in three sites and reaches the highest values (193 mg/kg) in two sites in the municipalities of Acerra and Marcianise respectively. The area with particularly high Pb values is, as expected, the area of Naples suburbs in which urbanization and related pollution (automobile traffic, industrial activities, etc.) is higher.


N
Pb - Lead
(mg/kg)
163 - 193
112 - 163
86 - 112
69 - 86
52 - 69
22 - 52
144 - 181
102 - 144
86 - 102
58 - 86
36 - 58
23 - 36
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Pb
Count
35
30
25
20
15
10
5
0
0
50
100
150
200
mg/kg


Pb
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
50
100
150
200
mg/kg

5b.19 Rubidium (Rb)

Rubidium is a metallic element of the alkali metals group.

It's used in very few fields, in the photocells production and in the removal of residual gases from vacuum tubes; its salts are used in fireworks and in glasses and ceramics production.

Rubidium and its salts have few commercial uses.

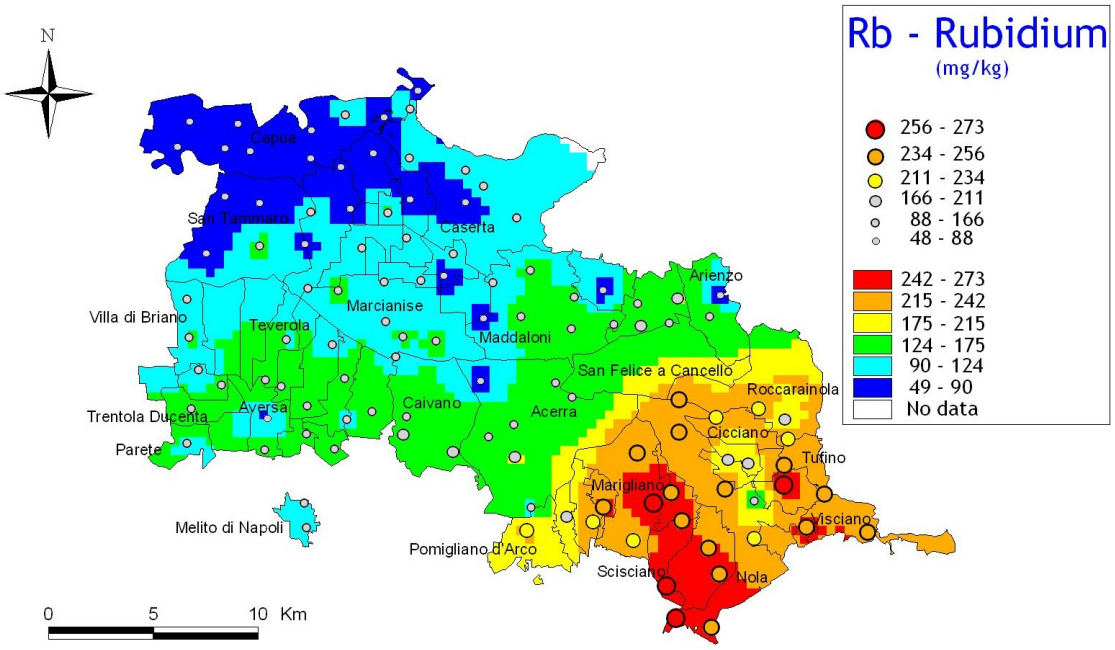
There are no rubidium minerals known, but it's present in significant amounts in minerals such as lepodite, pollucite and carnallite. It is also present in traces in trace amounts in other minerals such as zinnwaldite and leucite.

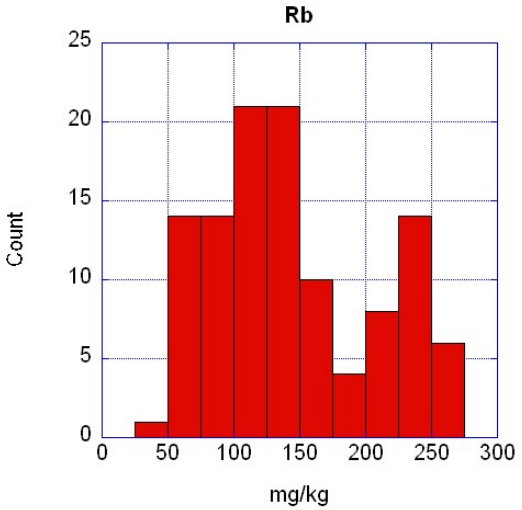
Rubidium has no known biological roles but overexposure may however cause problems to humans such as skin ulcers, nervousness, ataxia and hyper irritation.

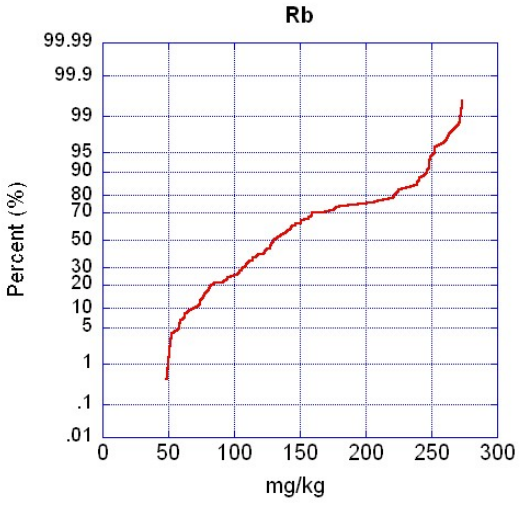
Plants quickly adsorb rubidium and, some of them, such as sugar beet, when affected by potassium deficiency can react with rubidium addition.

5b.19.1 Distribution of Rb concentrations

Rubidium contents in the analyzed soils range between 48 mg/kg and 273 mg/kg. Its distribution throughout all the investigated area follows a very regular pattern in which lowest values (49 mg/kg – 90 mg/kg) are found in the north-western part of the area, in Capua and San Tammaro, and the highest (256 mg/kg – 293 mg/kg) are found in the south-eastern part of it, in the municipalities of Nola, Saviano, Scisciano and Marigliano. This regular south-eastward increasing trend is strictly related to a strong geogenic source of rubidium in soils. As metal of the first group of the Periodic Table, it's very ubiquitous in all volcanic products of the Neapolitan area and, therefore, its high concentrations, have all a natural origin.


N
Rb - Rubidium
(mg/kg)
256 - 273
234 - 256
211 - 234
166 - 211
88 - 166
48 - 88
242 - 273
215 - 242
175 - 215
124 - 175
90 - 124
49 - 90
No data
Capua
San Tammaro
Caserta
Marcianise
Villa di Briano
Teverola
Maddaloni
Arienzo
San Felice a Cancello
Roccarainola
Aversa
Trentola Ducenta
Parete
Caivano
Acerra
Cicciano
Tufino
Marigliano
Visciano
Melito di Napoli
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Rb
Count
25
20
15
10
5
0
0
50
100
150
200
250
300
mg/kg


Rb
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
50
100
150
200
250
300
mg/kg

5b.20 Sulphur (S)

Sulphur is a multivalent non-metal. In nature it occurs as the pure element or as sulfide and sulfate minerals. The famous smell associated to this element is the main characteristic of hydrogen sulphide (H_2S).

Sulphur is used in batteries, manufacture of fertilizers, fungicides, gun powder, matches and fireworks.

It naturally occurs in volcanic environments; massive deposits are found in Texas and Louisiana in the USA. The most known sulphide minerals are pyrite and marcasite (iron sulphides) stibnite (antimony sulphide), galena (lead sulphide), cinnabar (mercury sulphide) and sphalerite (zinc sulphide). Other important sulphide ores are chalcopyrite, bornite and molybdenite. Canada is the main producer of sulphur for industry.

Sulphur has been a fundamental element for the development of life on Earth and still is necessary for all living things.

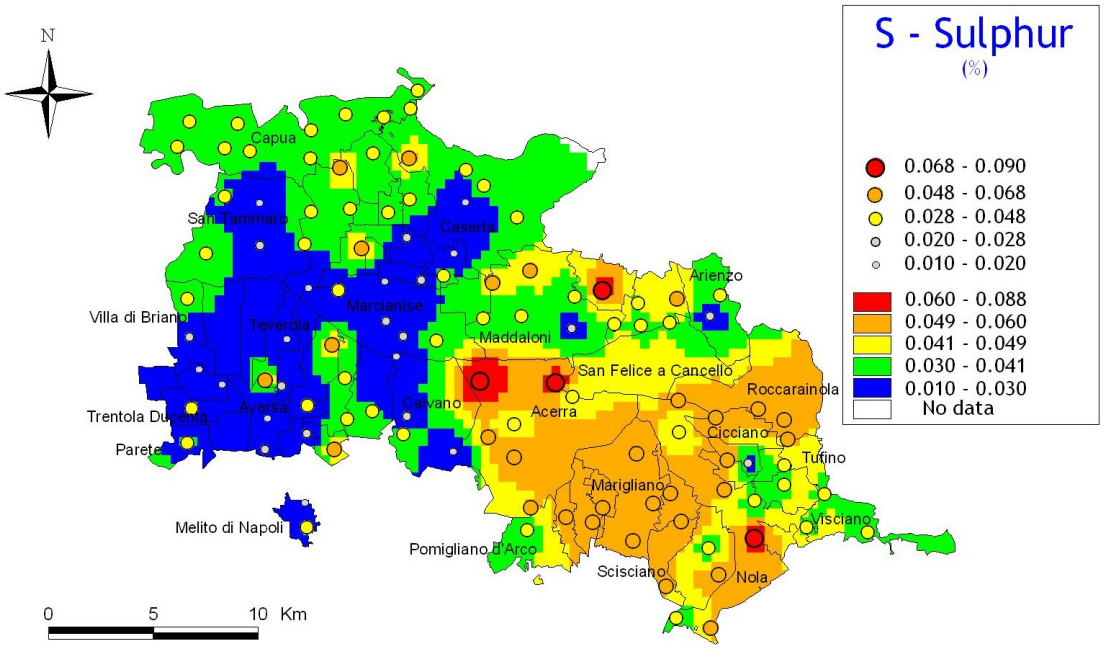
Elemental sulphur is non toxic, but many compounds, such as sulphur dioxide (SO_2) and hydrogen sulfide can be harmful.

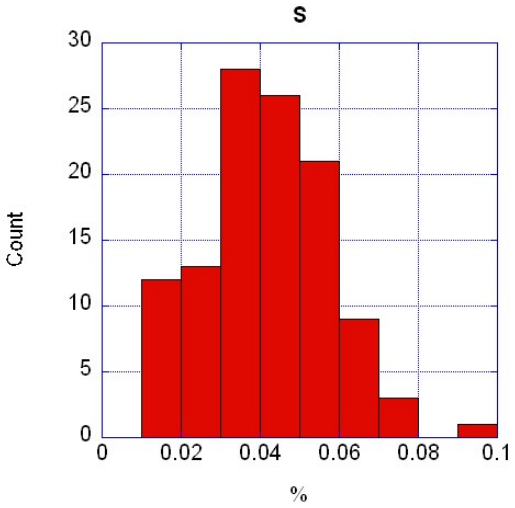
The main effects of sulphuric compounds on human health are: neurological problems, heart damage, reproductive failure, damage to liver and kidney functions, disturbance of the hormonal metabolism, dermatological effects, suffocation and lung embolism.

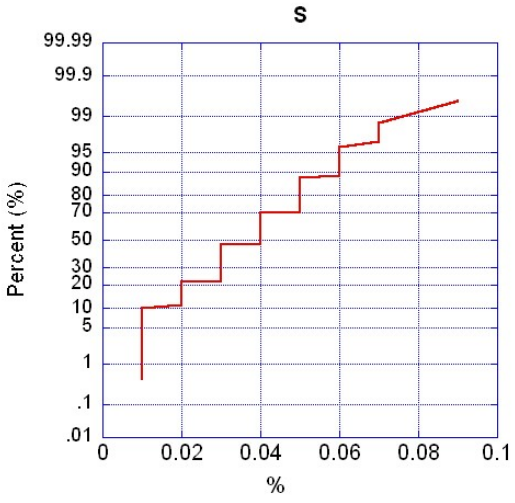
5b.20.1 Distribution of S concentrations

Sulphur contents vary from a minimum value of 0.01% to a maximum value of 0.09%. Very low (0.01% - 0.03%) sulphur concentrations in soils have been registered in the south-western corner of the investigated area, in the municipalities of Aversa, Teverola, Marcianise, and in part or most of the surrounding municipalities. Moving eastward concentrations found are high and very high (0.041% - 0.09%) but there isn't any gradual or regular increase of values. Peaks of maximum concentrations occur in Nola, in Cervino and in two sites sampled in the north of Acerra.

In the histogram most of the samples (about 75) have S concentrations between 0.03% and 0.06%; about 25 samples have lower values and 13 of them have S contents higher than 0.06%, up to the maximum value of 0.09%.


N
S - Sulphur
(%)
0.068 - 0.090
0.048 - 0.068
0.028 - 0.048
0.020 - 0.028
0.010 - 0.020
0.060 - 0.088
0.049 - 0.060
0.041 - 0.049
0.030 - 0.041
0.010 - 0.030
No data
Capua
San Tammaro
Caserta
Villa di Briano
Marcianise
Teverola
Arienzo
Maddaloni
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Carvano
Acerra
Cicciano
Paretè
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


S
Count
30
25
20
15
10
5
0
0
0.02
0.04
0.06
0.08
0.1
%


S
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
0.02
0.04
0.06
0.08
0.1
%

5b.21 Antimony (Sb)

Antimony is a semimetallic element with a low conductivity of heat and electricity.

Its compounds are used in paints, ceramics and pottery; its alloys are used in batteries while pure antimony is used to make diodes and infrared detectors.

Sometimes it's found free in nature, but is usually obtained from the ores stibnite (Sb_2S_3) and valentinite (Sb_2O_3). Antimony is an important economic metal and its main production countries are Russia, China, Bolivia and South Africa.

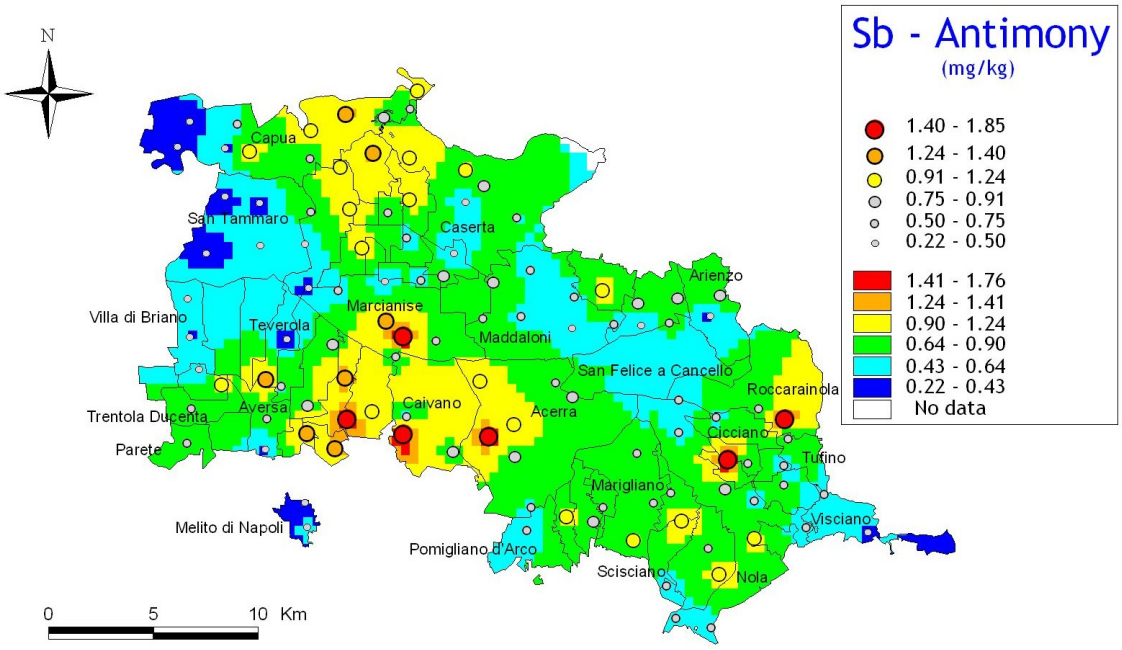
Antimony in the environment can be the result of both naturally occurring contents and several human activities.

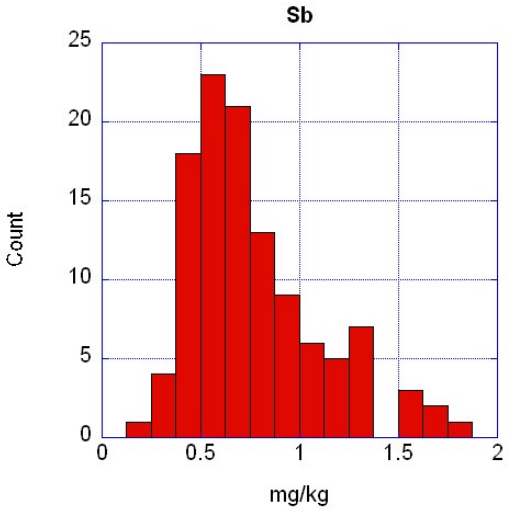
The main human exposure ways to Sb are breathing in its dusts, drinking waters and eating foods, but also skin contact with soils and waters containing it. Prolonged high Sb concentrations exposure can cause irritation of the eyes, skin and lungs. As the exposure continues more serious health effects may occur, such as lung diseases, heart problems, diarrhea, severe vomiting and stomach ulcers.

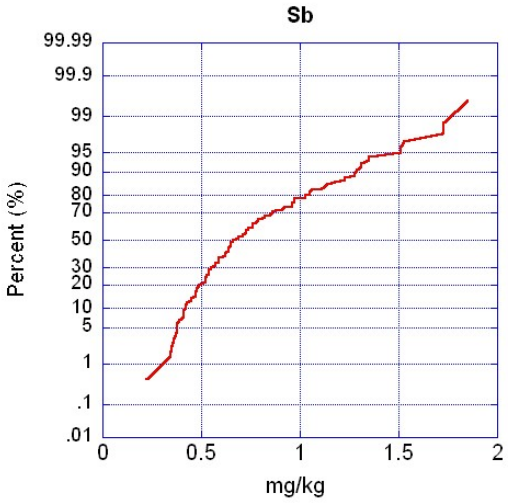
5b.21.1 Distribution of Sb concentrations

The antimony concentrations into the analyzed soil samples vary from a minimum value of 0.22 mg/kg, and a maximum value of 1.85 mg/kg. Its distribution pattern in the studied area shows higher concentrations (0.90 mg/kg – 1.85 mg/kg) especially in the central sector, both in the north (eastern Capua, San Prisco, northern Santa Maria Capua Vetere, Curti, western Caserta) and in the south (Acerra, Caivano, Marcianise, Succivo, Orta d'Atella, Sant'Arpino). Two sites in which very high Sb contents have been registered are Roccarainola and Cimitile. Low and moderately low Sb concentrations (0.22 mg/kg – 0.90 mg/kg) occur throughout all the investigated area without following any particular distribution pattern. The areas in which anomalies in Sb contents occur are randomly found in all the Agro Aversano, thus suggesting an anthropic origin of its contamination.

Antimony concentrations in soils of residential and industrial areas have been fixed by the 152/06 Environmental Law respectively at 10 mg/kg and 30 mg/kg. These limits are never reached in none of the analyzed samples, neither in the highest ones.


N
Sb - Antimony
(mg/kg)
1.40 - 1.85
1.24 - 1.40
0.91 - 1.24
0.75 - 0.91
0.50 - 0.75
0.22 - 0.50
1.41 - 1.76
1.24 - 1.41
0.90 - 1.24
0.64 - 0.90
0.43 - 0.64
0.22 - 0.43
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Sb
Count
25
20
15
10
5
0
0
0.5
1
1.5
2
mg/kg


Sb
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
0.5
1
1.5
2
mg/kg

5b.22 Selenium (Se)

Selenium is a non metallic element. The crystalline metal allotropic form, also known as metallic selenium, has a higher electrical conductivity in the light than in the dark, and is used in photocells.

Due to its good photovoltaic and photoconductive properties, it's widely used in electronics; other uses of selenium are in the glass industry, in rubbers vulcanization, for animal feeds and food supplements production, in photography and in metal alloys as the one used in rectifiers of AC-DC current.

The main selenium producing countries are Canada, USA, Bolivia and Russia.

Selenium can be released into the environment through both natural processes and human activities.

Agricultural soils on which phosphate fertilizers have been used, usually have high Se contents. The reaction of selenium with oxygen cause the element to be mobile and dissolve into water. Therefore in soils with high acidity, selenium is mobilized and, the chances of exposure to its compounds increase, becoming a threat for human health. High soils acidity is usually the result of human activities such as industrial and agricultural processes. Other parameters influencing selenium mobilization and its velocity are temperatures, moisture, organic matter content and microbial activity.

Human exposure to selenium can occur through food or water, or through contact with soil or air containing high concentrations of selenium. In foodstuffs such as grains, cereals and meat, selenium is naturally present.

It is an element necessary for humans in order to maintain good health. By the way, high and prolonged selenium exposure can cause the collection of fluid in the lungs and lead to bronchitis, but also chills, fever, headache, conjunctivitis, vomiting, abdominal pain and enlarged liver. Selenium shortages can cause heart and muscle problems. In some cases selenium poisoning may even lead to death.

Selenium can accumulate in the body tissues of organisms and can then be passed up through the biological cycle. Selenium contents tend to be very high in aquatic organisms in many areas because of the irrigation run-off from fertilized soils.

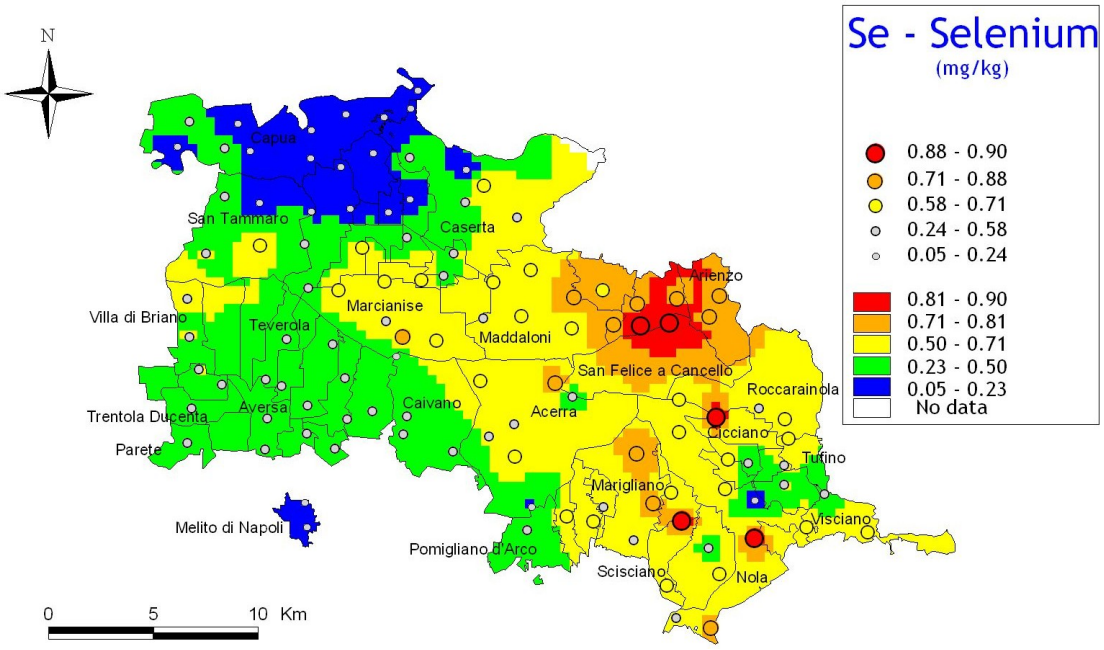
5b.22.1 Distribution of Se concentrations

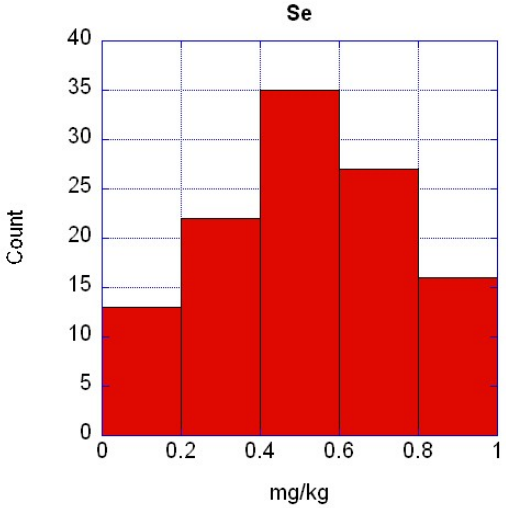
Selenium values in soils range between 0.05 mg/kg and 0.9 mg/kg. Lowest concentrations (0.05 mg/kg – 0.23 mg/kg) mainly occur in an area that includes most of Capua town, San Prisco, northern Santa Maria Capua Vetere and the north-eastern part of San Tammaro. A small area with very low Se contents is found in Melito di Napoli. In surrounding areas and in all the south-western part of the Agro Aversano, values slightly increase and range between 0.23 mg/kg and 0.50 mg/kg. Selenium concentrations become high in the north-eastern sector of the area and reach the highest contents (0.88 mg/kg – 0.90 mg/kg) in two sampling sites located between Santa Maria a Vico and San Felice a Cancello. Other sites in which registered Se concentrations rage between 0,88 mg/kg and 0.90 mg/kg are in Cicciano, in Nola and in Scisciano municipalities. These values seem to be related more

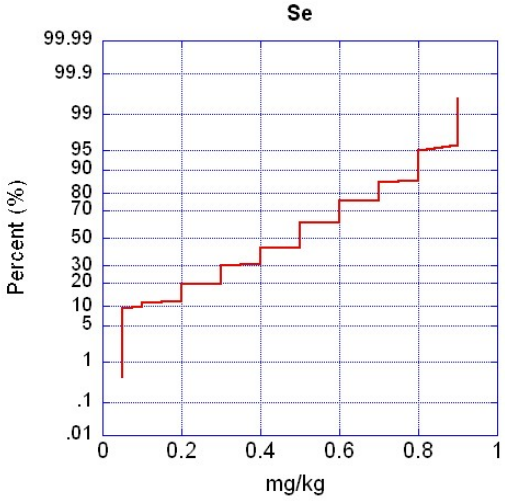
likely to different local sources of contamination and not to a geologic source as seem to be for the values found in the first area.

The distribution of selenium concentrations plotted in the histogram, identify a Gaussian-like curve, with a maximum amount of samples (35) in the interval between 0.4 mg/kg and 0.6 mg/kg.

According to the 152/06 Italian Environmental Law, selenium contents in soils should not exceed 3 mg/kg in residential areas and 15 mg/kg in industrial areas; the values registered in the analyzed soils are always lower than these limits.


N
Se - Selenium
(mg/kg)
0.88 - 0.90
0.71 - 0.88
0.58 - 0.71
0.24 - 0.58
0.05 - 0.24
0.81 - 0.90
0.71 - 0.81
0.50 - 0.71
0.23 - 0.50
0.05 - 0.23
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Aversa
Caivano
Acerra
Trentola Ducenta
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Se
Count
40
35
30
25
20
15
10
5
0
0
0.2
0.4
0.6
0.8
1
mg/kg


Se
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
0.2
0.4
0.6
0.8
1
mg/kg

5b.23 Tin (Sn)

Tin is a soft metal. It is used, as alloy with other metals in electrical circuits, in superconducting magnets, in dental amalgam, while its oxide is used for ceramics and in gas sensors.

Due to the insolubility and the high weathering resistance of its oxide, tin contents in soils and natural waters is quite low. Soils concentrations usually vary between 1 and 4 ppm, even if, in some particular areas, contents may be lower than 0.1 ppm or even about 300 ppm (peats).

The only economic tin mineral is cassiterite; its main mining area, also known as the "tin belt", goes from China through Thailand and Malaysia to Indonesia.

Tin is not a toxic substance in its metallic form, but becomes very harmful for living organisms in its organic compounds. Despite the well-known toxicity of organic tin, these compounds are still applied in many uses such as the paint industry, the plastic industry, and in agriculture through pesticides.

The uptake of tin bonds by the humans may occur through food and breathing and through skin contact. The effects of tin bonds exposure can be: eye and skin irritations, headaches, stomachaches, but also depressions, liver damage, shortage of red blood cells and brain damage.

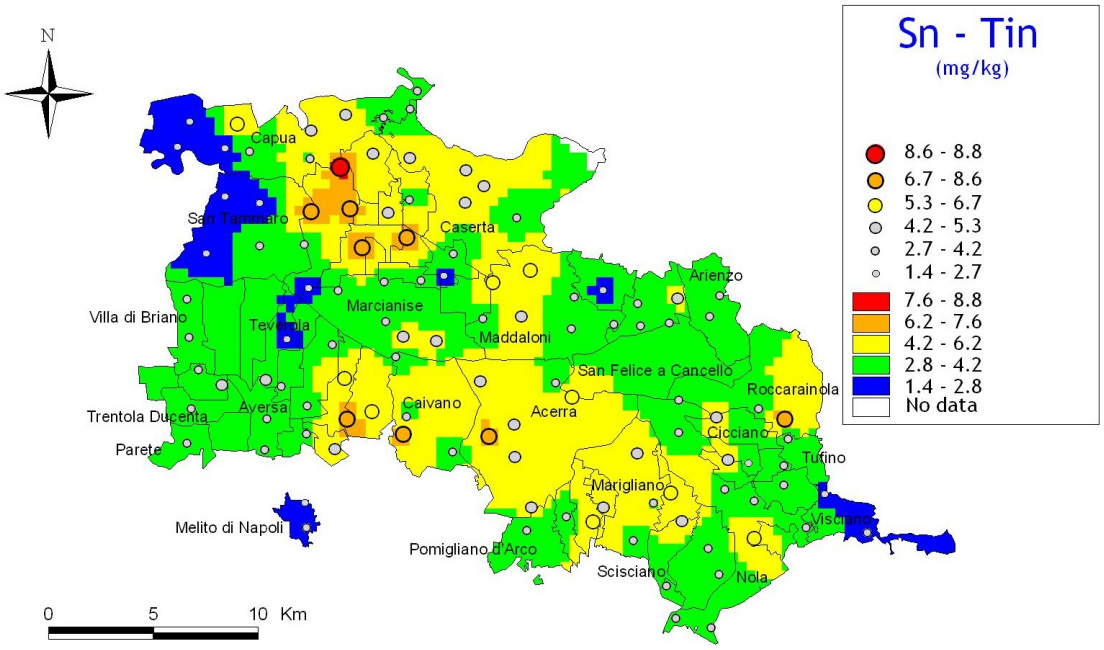
Organic tins can be adsorbed on sludge particles and spread through the water systems; they are very harmful for aquatic organisms and related ecosystem, as they are very toxic to fungi, algae and phytoplankton.

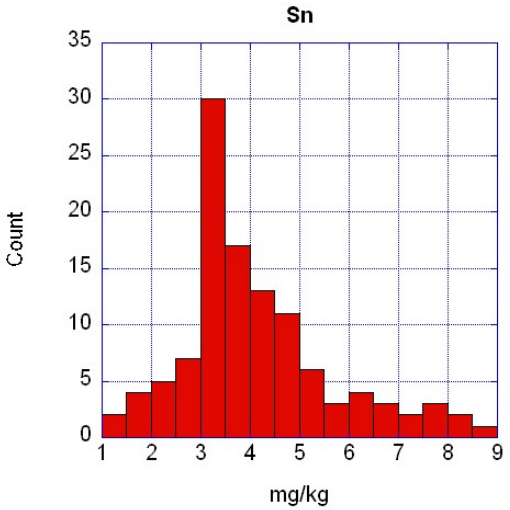
5b.23.1 Distribution of Sn concentrations

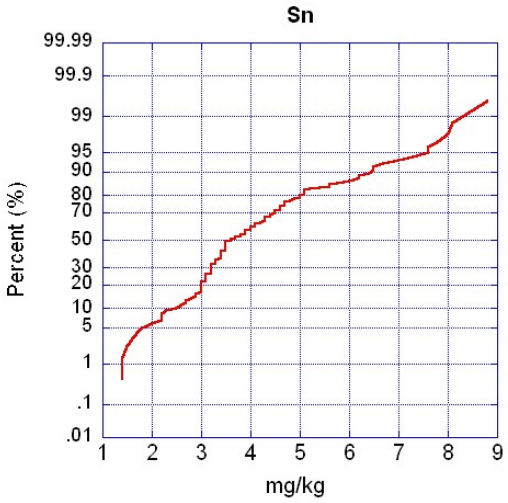
Tin contents in the investigated area range from a minimum value of 1.4 mg/kg and a maximum value of 8.8 mg/kg. Lowest concentrations (1.4 mg/kg – 2.8 mg/kg) occur in few and small areas respectively found in western Capua and San Tammaro towns, in Melito di Napoli and in Visciano. Relatively high Sn concentrations (6.7 mg/kg – 8.6 mg/kg) are registered in isolated sampling sites in Roccarainola, Caivano, Acerra and Orta d'Atella, and in a small area around Santa Maria Capua Vetere, where is also found the highest Sn value registered (8.8 mg/kg).

In the histogram and in the cumulative frequency curve is shown that most of the samples have Sn concentrations below 5.5 mg/kg, and 30 of them are comprised in the interval between 3 mg/kg and 3.5 mg/kg.

Tin is one of the element for which Italian Environmental Law, has fixed an intervention limit. Its limits are 1 mg/kg for areas with a residential destination, and 350 mg/kg for areas with an industrial destination. As shown by the geochemical map, throughout the whole Agro Aversano, the lower limit, relative to the residential use, is always exceeded.


N
Sn - Tin
(mg/kg)
8.6 - 8.8
6.7 - 8.6
5.3 - 6.7
4.2 - 5.3
2.7 - 4.2
1.4 - 2.7
7.6 - 8.8
6.2 - 7.6
4.2 - 6.2
2.8 - 4.2
1.4 - 2.8
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Sn
Count
35
30
25
20
15
10
5
0
1
2
3
4
5
6
7
8
9
mg/kg


Sn
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
1
2
3
4
5
6
7
8
9
mg/kg

5b.24 Strontium (Sr)

Strontium is an alkaline-earth metal. Its physical and chemical properties are similar to those of calcium and barium and, for this reason, most of its applications are the same as calcium and barium ones.

Strontium compounds main uses are in pyrotechnics, in vacuum tubes and for television screens production. Strontium-90 is a dangerous radioactive isotope, but its high-energy radiation is used to generate an electric current in space vehicles, remote weather stations and navigation buoys.

Strontium is commonly found in nature as celestite ($SrSO_4$) and strontianite ($SrCO_3$). The major mining areas are UK, Mexico, Turkey and Spain.

The main ways through which strontium may be absorbed by human body are eating and drinking. Some of the food containing high strontium concentrations are grains, dairy products, leafy vegetables, cabbages and onions. Drinking waters may be contaminated by water-soluble strontium when the insoluble form changes as a result of chemical reactions. Water-soluble strontium compounds are more toxic for human health than the water-insoluble ones.

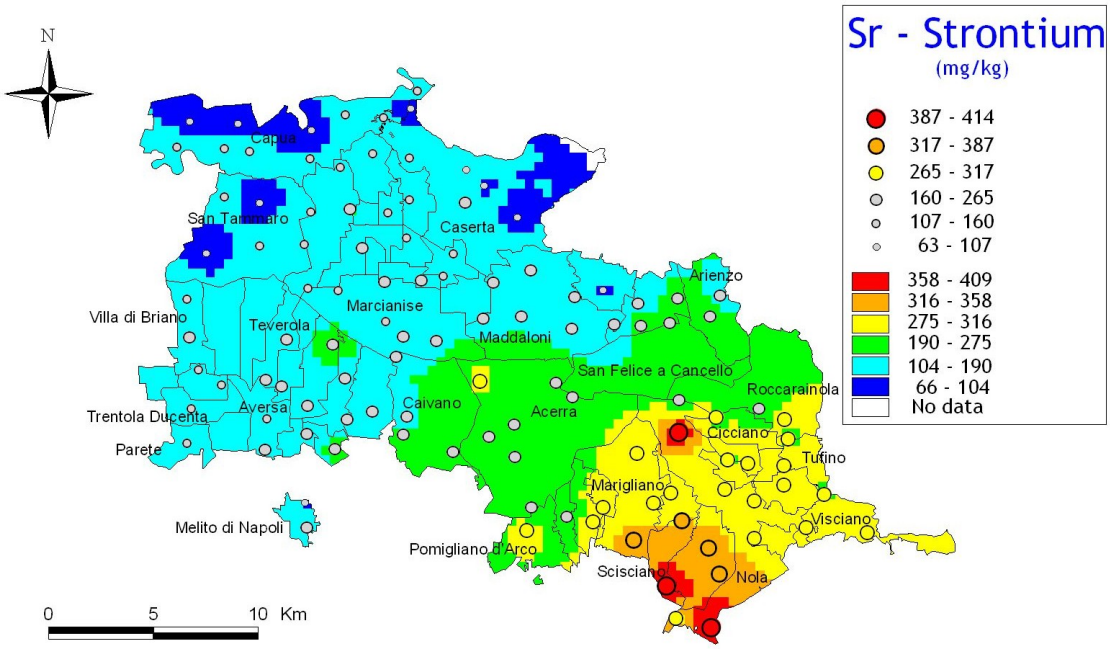
There are no particular dangers for human health in the uptake of high strontium concentrations, but, for extremely high concentrations bones problems may occur. Radioactive strontium is much more a health risk than its stable form; it may cause anemia, oxygen shortages, and even cause cancer.

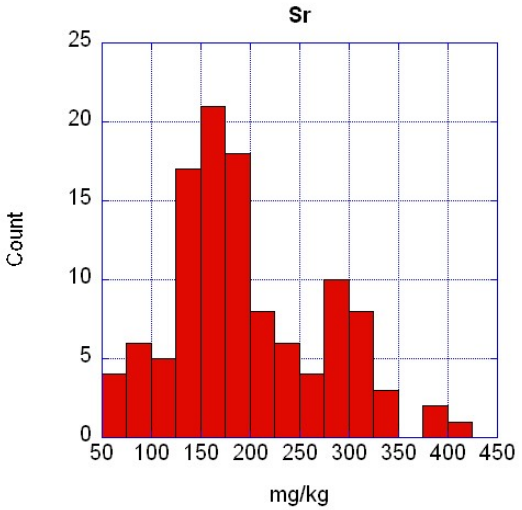
Human activities that introduce strontium into the environment are coal and oil combustion, dumping and industrial wastes. Dusts that contain strontium will settle to surface water, soils or plant surfaces. Radioactive strontium isotope doesn't naturally occur into the environment; it usually derives from human activities such as radioactive storage leaking and nuclear bomb testing.

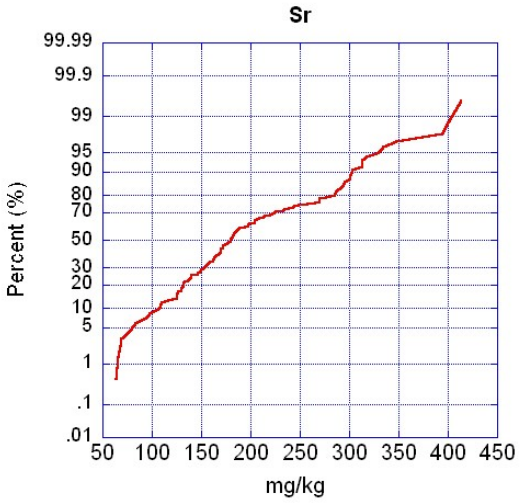
5b.24.1 Distribution of Sr concentrations

Strontium values in the soils of the investigated area vary between 63 mg/kg and 414 mg/kg. Its distribution pattern is the same as those of all the other metals belonging to the first and second group of the Periodic Table of the elements. Values follow a regular increasing trend moving south-eastward from a minimum concentration area (66 mg/kg – 104 mg/kg) located in western Capua and San Tammaro. The highest values registered (387 mg/kg – 414 mg/kg) occur in southern Scisciano and southern Nola; a sample with these values is also found in one site in the northern part of Nola.

As for all the other alkali and earth-alkali metals, also Sr concentrations in soils are strictly related to the volcanism of the Neapolitan area.


N
Sr - Strontium
(mg/kg)
387 - 414
317 - 387
265 - 317
160 - 265
107 - 160
63 - 107
358 - 409
316 - 358
275 - 316
190 - 275
104 - 190
66 - 104
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Sr
Count
25
20
15
10
5
0
50 100 150 200 250 300 350 400 450
mg/kg


Sr
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
50 100 150 200 250 300 350 400 450
mg/kg

5b.25 Thorium (Th)

Thorium is a metal whose oxide has a melting point of 3300°C, one of the highest of all oxides.

Thorium is a source of nuclear power, much of the earth internal heat has been attributed to thorium and uranium.

Before the discovery of the threats related to thorium radioactivity, it was used, along with its compounds, in many fields such as in gas mantles, and in toothpaste. Thorium is still used as an alloying element in magnesium, for high-temperature laboratory crucibles, and to increase special glasses refractivity. In the scientific world Th is used with uranium to date fossils.

Thorium in the Earth's crust is almost as abundant as lead and three times more abundant than uranium. It is found in small amounts in most rocks and soils but, due to its oxide high insolubility, very little of this element is found into the environment. Thorium minerals naturally occurring are thorite, uranothorite, and thorianite; it is a major component of monazite and it is present in significant amounts in the minerals zircon, titanite, gadolinite and betafite.

Thorium is almost everywhere on earth and, therefore, humans are continuously exposed to small amounts of thorium through air, food and water, but these contents are so small to not be considered dangerous.

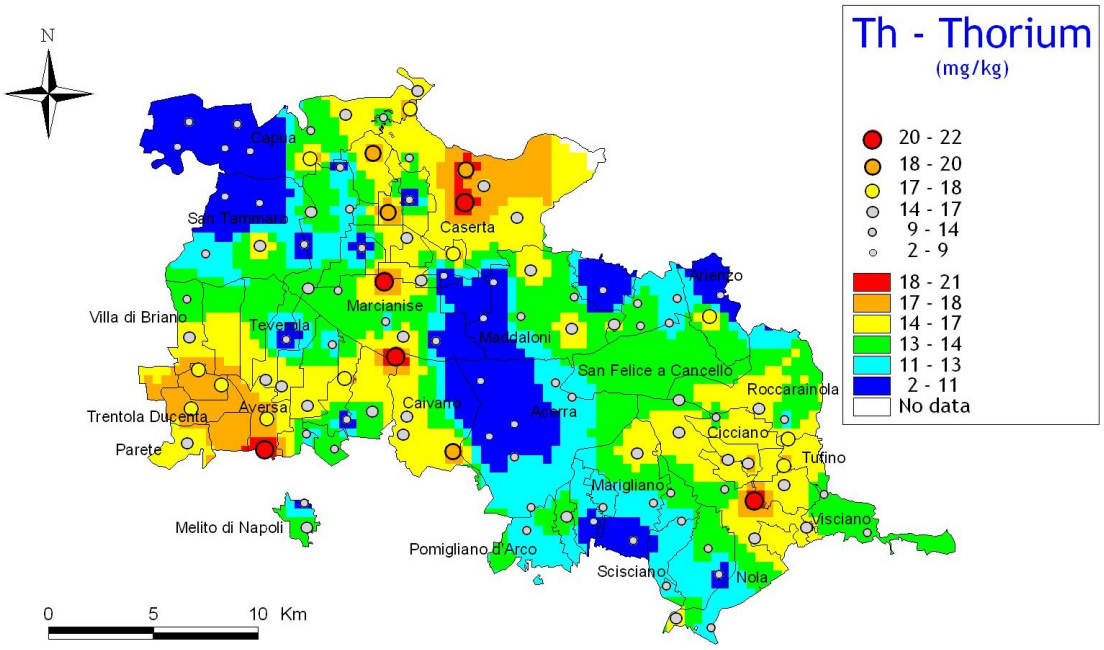
Very high thorium contents can be found near hazardous waste sites and can represent a threat for people living nearby who breathe its dusts and eat food grown on contaminated soils.

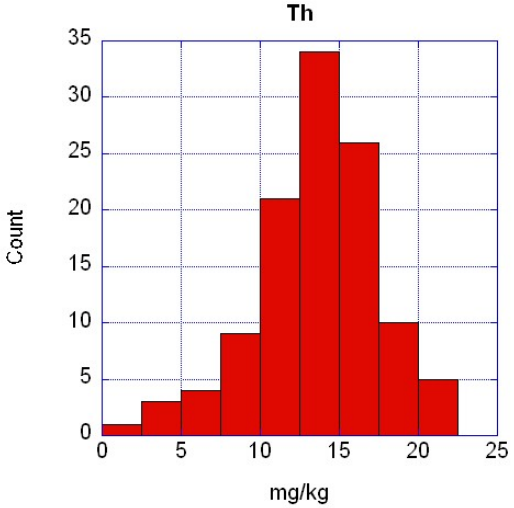
Breathing in high thorium contents for long periods may be lethal; chances of development of lung diseases and lung and pancreas cancer increase. Thorium has the ability to change genetic materials, it’s radioactive and can be stored in bones and also cause bone cancer.

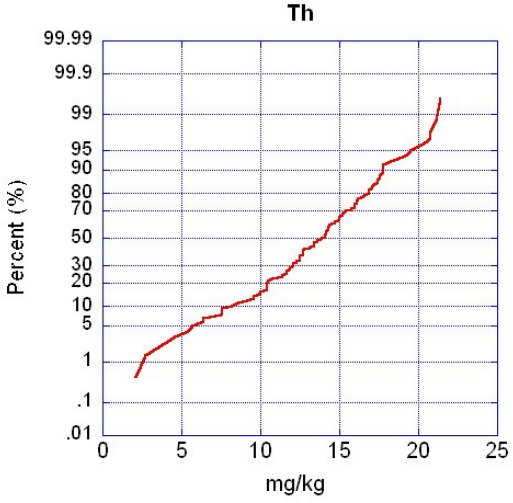
5b.25.1 Distribution of Th concentrations

In the soils of the Agro Aversano, thorium concentrations vary from 2 mg/kg, to 22 mg/kg. Its contents throughout the area are not regularly distributed, low and very low values (2 mg/kg – 13 mg/kg) are found in western Capua and Northern San Tammaro, in a central area that includes part of Maddaloni and Marcianise, most of Acerra and part of Scisciano, Marigliano and Nola, and in some other isolated and randomly distributed points. Areas in which interpolated values are higher than 17 mg/kg, are found in northern Caserta town and to the west of Aversa. In these areas are found some of the highest Th concentrations (22 mg/kg – 22 mg/kg) which also occur in Marcianise, To the north of Caivano and in Nola.

The irregular distribution of both high and low Th contents seem to have no particular geologic origin.


N
Th - Thorium
(mg/kg)
20 - 22
18 - 20
17 - 18
14 - 17
9 - 14
2 - 9
18 - 21
17 - 18
14 - 17
13 - 14
11 - 13
2 - 11
No data
Capua
San Tammaro
Caserta
Marcianise
Villa di Briano
Teverola
Maddaloni
Arienzo
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Carinaro
Aderra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Th
Count
35
30
25
20
15
10
5
0
0
5
10
15
20
25
mg/kg


Th
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
5
10
15
20
25
mg/kg

5b.26 Titanium (Ti)

Titanium is a transition metal that shows many physical and chemical similarities with that of silica and zirconium.

Its dioxide is widely used as a white pigment in outside paintings; once it was also used as a bleaching and opacifying agent in porcelain enamels.

Titanium alloys, because of their high strength and very low weight, are mainly used in aircraft, pipes for power plants, naval ships, spacecraft and missiles.

In medicine titanium is used to make hip and knee replacements, pace-makers, bone-plates and screws and cranial plates for skull fractures. It has also been used to attach false teeth.

In nature titanium is present in most igneous rocks and in related sediments. Its main minerals are rutile, titanite brookite, ilmenite, and anatase. The major ore is ilmenite and the main countries in which it is mined are Western Australia, Canada, Norway and Ukraine where it occurs as vast deposits of sand. In North America and South Africa large rutile deposits occur and their mining significantly contribute to the world supply of titanium.

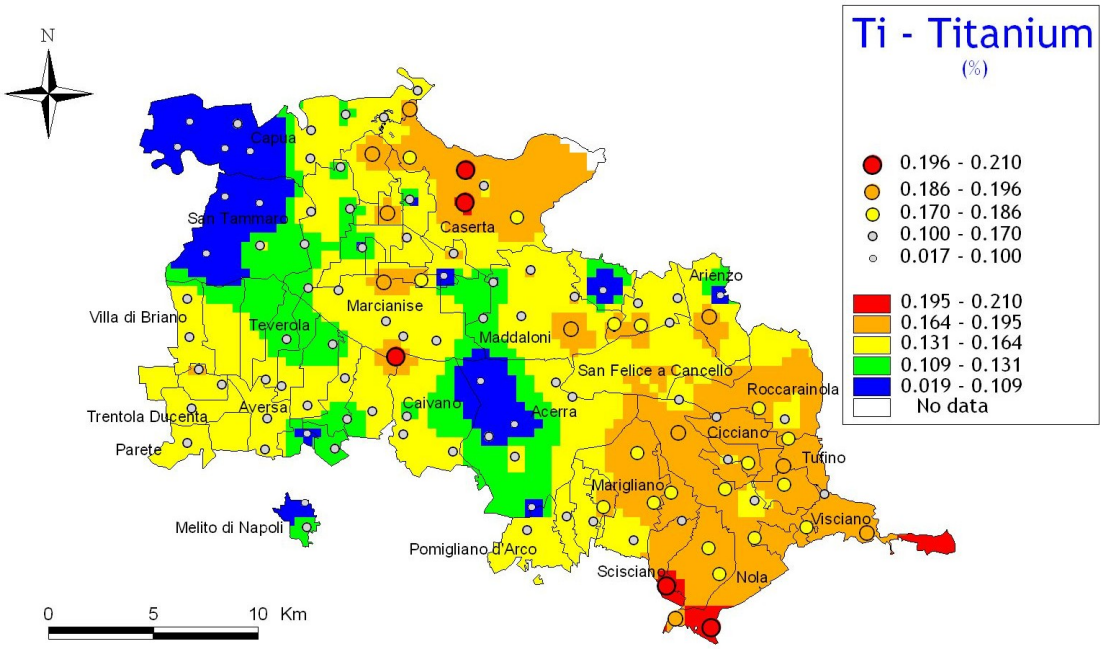
Both elemental and titanium dioxide have very low toxicity. It's not a poison metal and the human body can tolerate titanium even in large doses. Most of the titanium that humans uptake through breathing, eating and drinking, isn't absorbed by the body, it usually simply passes through.

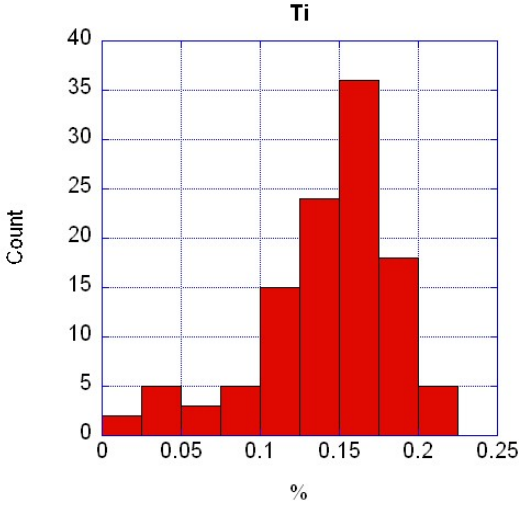
5b.26.1 Distribution of Ti concentrations

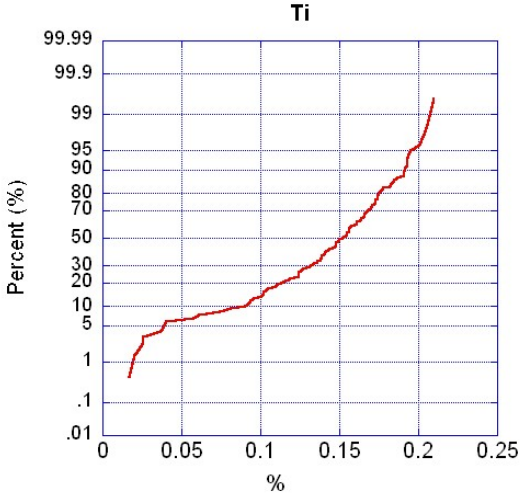
Titanium values in the analyzed soils of the Agro Aversano vary in a range between 0.019% and 0.210%. The areas in which lowest concentrations occur, are found in Capua, San Tammaro and in Acerra municipalities. Areas with high and relatively high Ti contents (>0.164 mg/kg) are the Caserta town and almost all of the eastern sector of the investigated area. The maximum Ti values (0.196 mg/kg – 0.210 mg/kg) have been registered in two sampling sites in Caserta, between Marcianise and Acerra and to the south of Scisciano and Nola.

As shown by the histogram and the cumulative frequency curve, most of the analyzed soil samples have Ti concentrations higher than 0.1%, with a peak of samples (35) in the interval between 0.15% and 0.175%.

The very high Ti values found both in Caserta town and near the Vesuvius area, could be due to a geogenic control of volcanic origin, but probably, the very high value found near Marcianise, is related to a local source of human contamination.


N
Ti - Titanium
(%)
0.196 - 0.210
0.186 - 0.196
0.170 - 0.186
0.100 - 0.170
0.017 - 0.100
0.195 - 0.210
0.164 - 0.195
0.131 - 0.164
0.109 - 0.131
0.019 - 0.109
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Sciscian
Nola
0
5
10 Km


Ti
Count
40
35
30
25
20
15
10
5
0
0
0.05
0.1
0.15
0.2
0.25
%


Ti
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
0.05
0.1
0.15
0.2
0.25
%

5b.27 Thallium (Tl)

Thallium is a metal very soft and malleable.

Due to its low melting point it's used in special glass production and in thermometers for low temperature. Other uses are: in photocells, for sink-float separation of minerals, as reagent in chemical research, as rat poison and as a pesticide in developing countries (its sulphate is banned in western countries).

Thallium minerals are rare, it is mainly found in potassium minerals such as sylvite and pollucite.

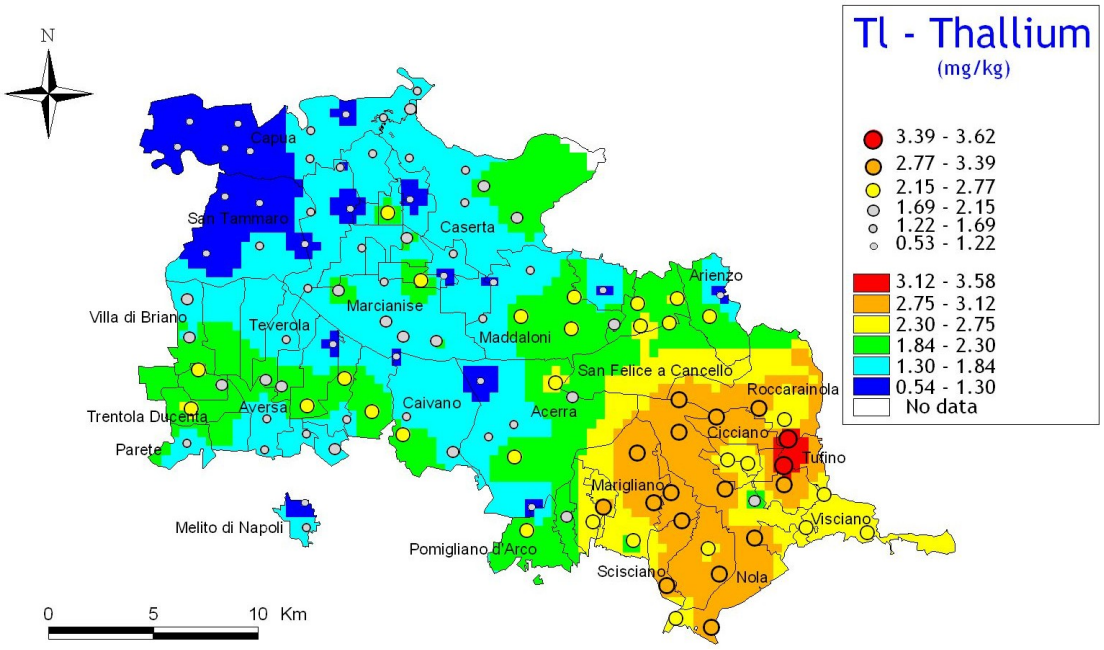
Into the environment thallium can spread by water mobilization from Tl-rich soils to groundwaters.

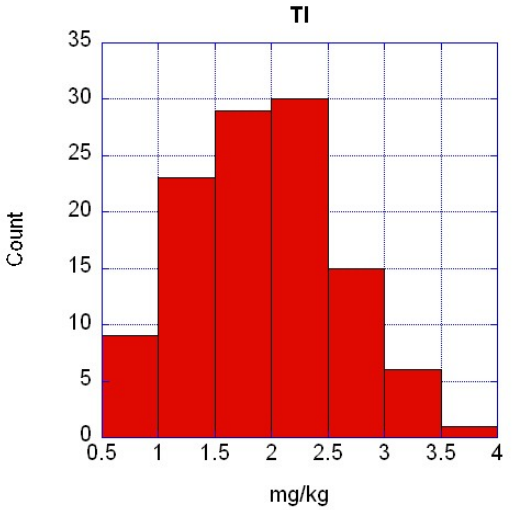
Thallium and its compounds are highly toxic. Human body can absorb thallium through skin, breathing organs and digestive tract, its uptake mainly occur after accidental contact or ingestion of rat poison. Poisoning effects are stomachaches and nervous systems damages and, in some cases even death. Chronic effects of thallium accumulation in human bodies are depressions, leg pains, hair loss, headaches, and lack of appetite.

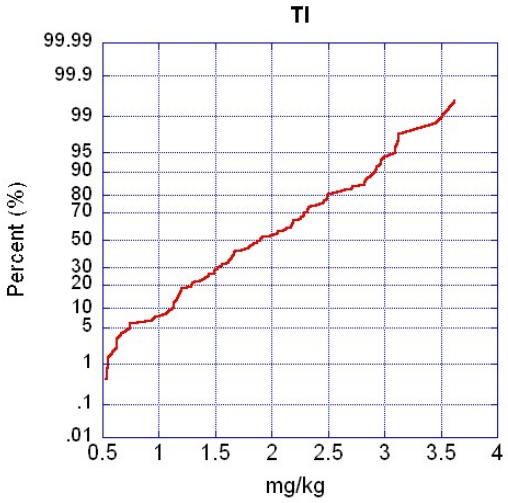
5b.27.1 Distribution of Tl concentrations

Thallium values in soils range from a minimum of 0.54 mg/kg and a maximum of 3.62 mg/kg. Its lowest values (0.54 mg/kg – 1.30 mg/kg) are found in Capua and San Tammaro, but relatively low values, up to 1.84 mg/kg, are found in all the central sector of the area, from Santa Maria Capua Vetere to western borders of Acerra and Maddaloni. Here Tl contents start increase toward east (2.30 mg/kg – 3.12 mg/kg) and reach the highest values in two points located in Tufino.

Thallium concentration limits in soils have been fixed by the 152/06 Environmental Law and, according to it, Tl contents should not exceed 1 mg/kg in residential areas and 10 mg/kg in industrial areas. As shown not only by the geochemical map, but also by the statistical graphs realized, only 9 of 113 sampled soils do not exceed the limit fixed for residential land use.


N
Tl - Thallium
(mg/kg)
3.39 - 3.62
2.77 - 3.39
2.15 - 2.77
1.69 - 2.15
1.22 - 1.69
0.53 - 1.22
3.12 - 3.58
2.75 - 3.12
2.30 - 2.75
1.84 - 2.30
1.30 - 1.84
0.54 - 1.30
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Tl
Count
mg/kg
0
5
10
15
20
25
30
35
0.5
1
1.5
2
2.5
3
3.5
4


Tl
Percent (%)
mg/kg
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0.5
1
1.5
2
2.5
3
3.5
4

5b.28 Uranium (U)

Uranium is a radioactive metal with a very high density.

Its importance has grown with the use of nuclear energy. In the military industry it is used in bullets and missiles, but also as shield to protect tanks; in the civilian sector uranium is used to fuel nuclear power plants and is also contained in many phosphate fertilizers.

Uranium is widely spread throughout the environment: in rocks, soil, air and water. In waters uranium is the result of rocks weathering, in air and soils contents usually are quite low. The anthropic contribution to the uranium contents into the environment are mainly the industrial activities and the mine and mills disposals.

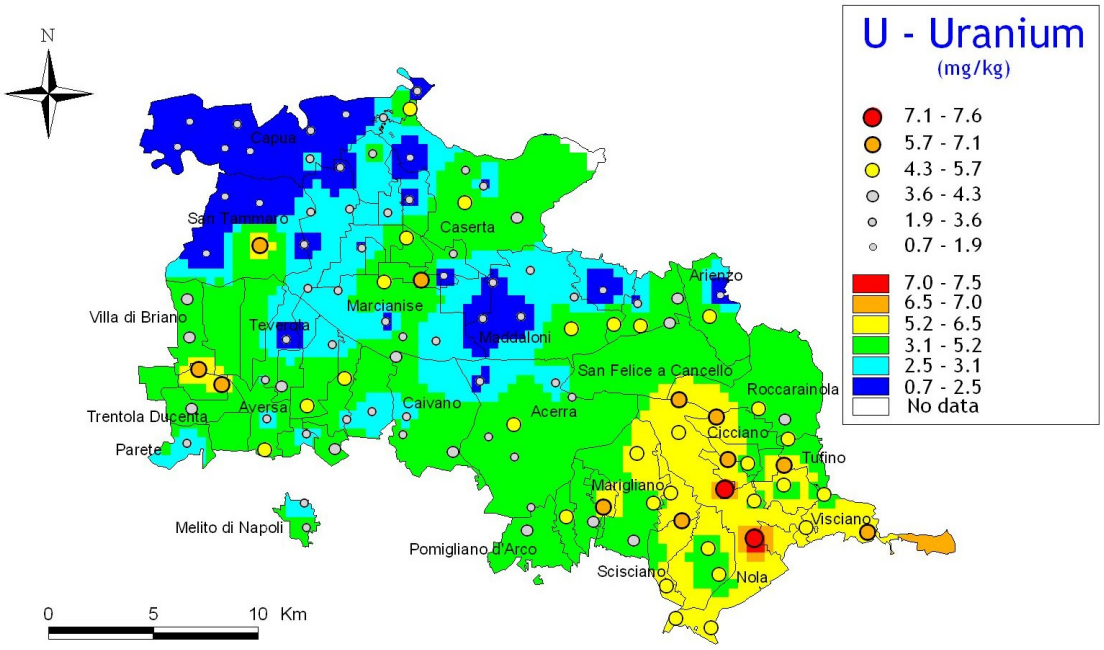
High exposure to uranium may be mainly experienced by people living near contaminated areas, such as mines and hazardous waste sites and by people working in the phosphate industry.

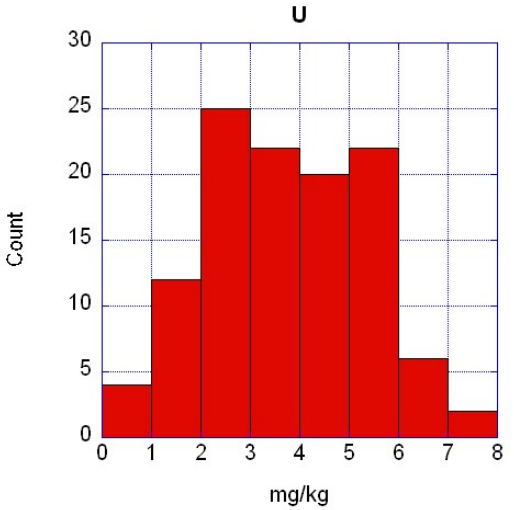
Natural uranium concentrations are not considered to be harmful for human health; however high and prolonged exposure to uranium radionuclides, especially to enriched uranium (a high radioactive form) can increase the chances to develop cancer.

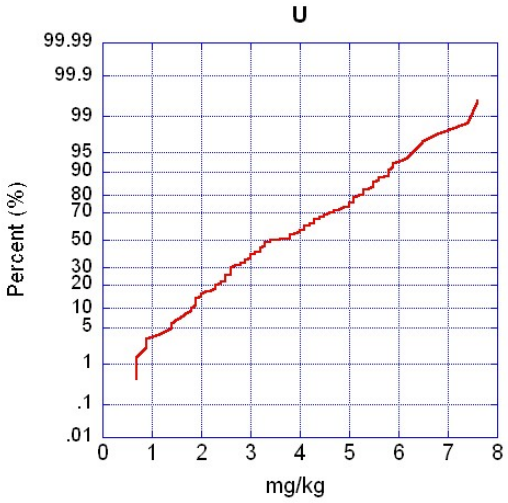
5b.28.1 Distribution of U concentrations

In the soils of the studied area, uranium contents vary from 0.7 mg/kg to 7.6 mg/kg. Lowest concentrations (0.7 mg/kg – 3.1 mg/kg) are mostly found in Capua and San Tammaro and their surrounding areas, but also occur in Maddaloni and Arienzo. In the south-easternmost sector of the area values increase (>5.2 mg/kg) and reach the maximum concentrations (7.1 mg/kg – 7.6 mg/kg) in two points in Nola. Sites in which the sampled soils have values between 5.7 mg/kg and 7.1 mg/kg are also found in one point to the south of San Tammaro, in two sites in San Marcellino, and in one point to the north of Marcianise.

The high values found to the south of the Agro Aversano could be more likely related to a geologic source of the element; on the other hand the high concentrations found in the other sites probably are due to anthropic local sources of pollution.


N
U - Uranium
(mg/kg)
7.1 - 7.6
5.7 - 7.1
4.3 - 5.7
3.6 - 4.3
1.9 - 3.6
0.7 - 1.9
7.0 - 7.5
6.5 - 7.0
5.2 - 6.5
3.1 - 5.2
2.5 - 3.1
0.7 - 2.5
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


U
Count
mg/kg


U
Percent (%)
mg/kg

5b.29 Vanadium (V)

Vanadium is a metal mainly used to produce alloys.

Its alloys are used in jet engines and high speed air-frames, in nuclear reactors, in axles, gears crankshafts and other components.

Vanadium occurs in many different minerals, the most famous of these are vanadinite, patronite, carnotite and bauxite. It's always obtained as a byproduct of other ores even if many vanadium ores are known.

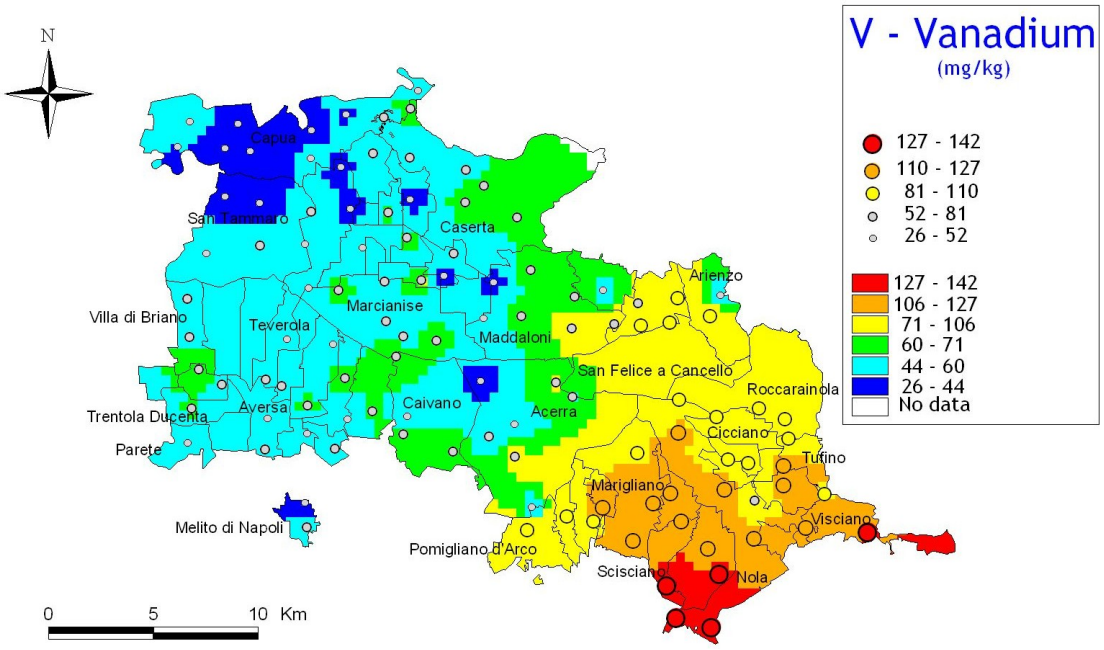
Vanadium is contained even in large concentrations in most soils and, according to its availability, is absorbed by plants. Humans mainly uptake vanadium through food; the vanadium richest are soya, beans, eggs, apples, olive oil and sunflower oil.

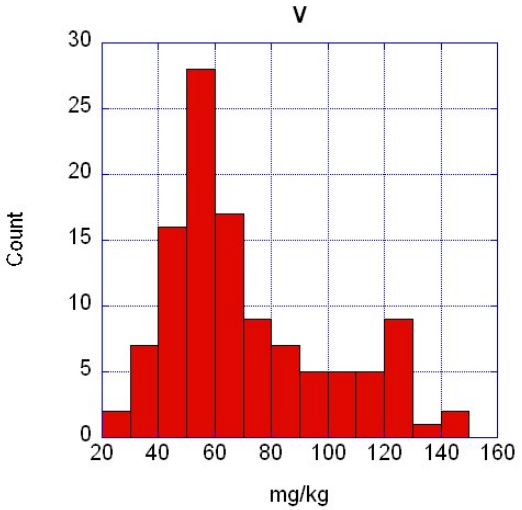
Vanadium effects on human health, for high exposure, are bronchitis and pneumonia, irritation of lungs, throat, eyes and nasal cavities, cardiac and vascular disease, inflammation of stomach and intestines, damage to the nervous system, bleeding of livers and kidneys, severe trembling and paralyses, weakening, and headaches.

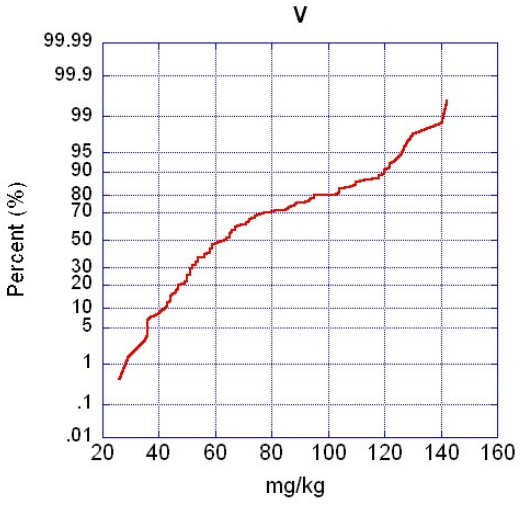
5b.29.1 Distribution of V concentrations

Vanadium concentrations in the soils of the Agro Aversano vary in a range from 26 mg/kg and 142 mg/kg. Its distribution pattern trough the area suggests a strong influence of a geologic volcano-related source, and in particular, of the Somma-Vesuvio complex volcanic activity. In this pattern low and very low values (26 mg/kg – 60 mg/kg) occur in the north-western sector of the area and then increase moving toward the south-eastern sector of it. Near Marigliano values become higher than 106 mg/kg and reach the maximum concentrations in five points: four of these are located to the south of Nola and Scisciano and one is found in Visciano.

According to the Environmental Law 152/06, vanadium concentration limits in soils with a residential destination is 90 mg/kg, in soils with an industrial destination in 250 mg/kg. The lower limit of 90 mg/kg is exceeded in almost 80% of the collected samples, as shown by the cumulative frequency curve.


N
V - Vanadium
(mg/kg)
127 - 142
110 - 127
81 - 110
52 - 81
26 - 52
127 - 142
106 - 127
71 - 106
60 - 71
44 - 60
26 - 44
No data
Capua
San Tammaro
Caserta
Arienzo
Villa di Briano
Marcianise
Teverola
Maddaloni
San Felice a Cancello
Roccarainola
Trentola Ducenta
Aversa
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Sciscian
Nola
0
5
10 Km


V
Count
30
25
20
15
10
5
0
20
40
60
80
100
120
140
160
mg/kg


V
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
20
40
60
80
100
120
140
160
mg/kg

5b.30 Zinc (Zn)

Zinc is a metal used in many and different fields: from coins to gutters, from iron galvanization to paints, from cosmetics to photocopier paper.

Its main ore is the blende (or sphalerite), but also smithsonite and hemimorphite; its major mining districts are Russia, USA, Canada, Australia and Peru.

Zinc naturally occurs in many foodstuffs and in drinking water. In soils, air and waters, it can be naturally found, but human activities such as coal and waste combustion, mining and steel production, may be sources of zinc contamination.

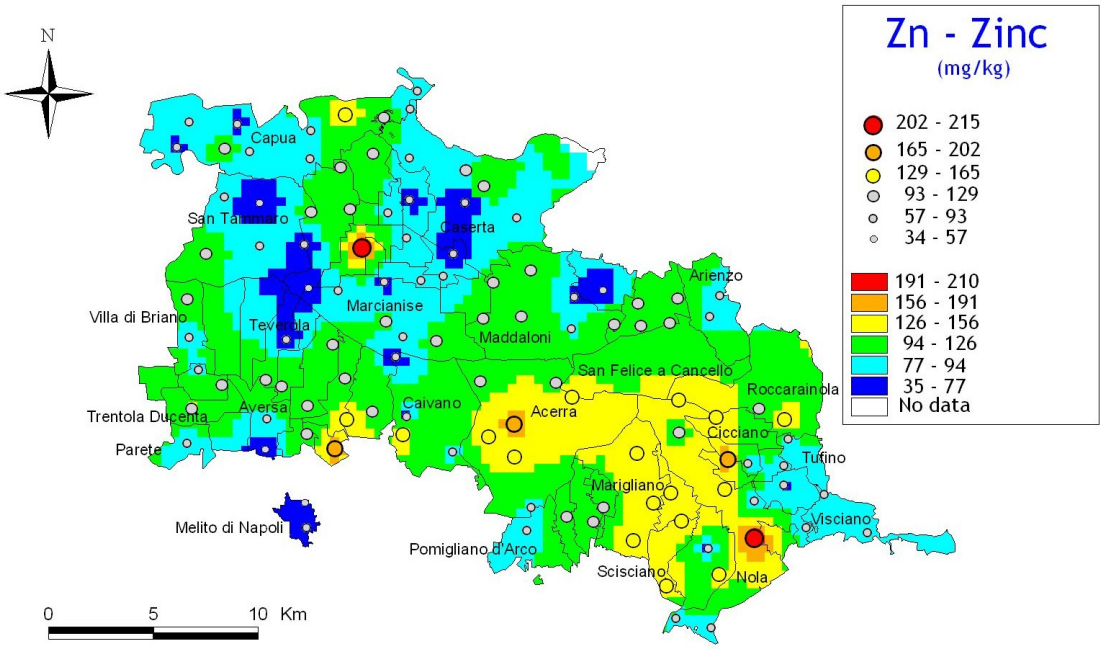
It is a trace element essential for human health and, therefore, people with zinc shortages can have some problems, such as loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. On the other hand, too much zinc can cause health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia, but also pancreas damages and arteriosclerosis.

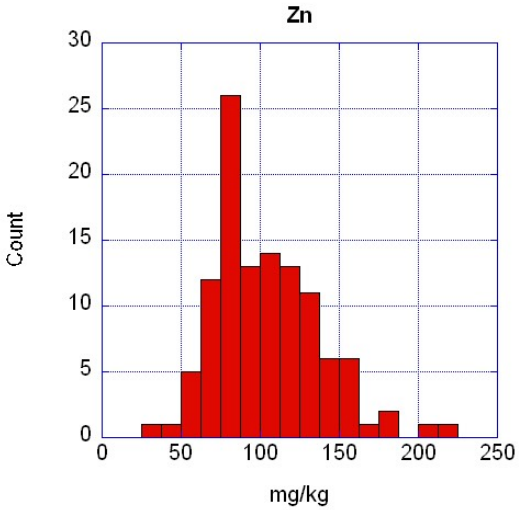
Zinc can contaminate rivers and seas when released by industries into the wastewaters; as a consequence, acidity of waters increases, and water organisms may accumulate it in their bodies. Some fish uptake zinc from waters and bio magnify it up the food chain. Animals and plants living on Zn-rich soils can also uptake it and this negatively influences the plants diversity because only few species of them can survive high Zn accumulation. The presence of large zinc contents in soils can also interrupt the activity of microrganisms and earthworms, thus causing serious problems to the evolution of the soil itself.

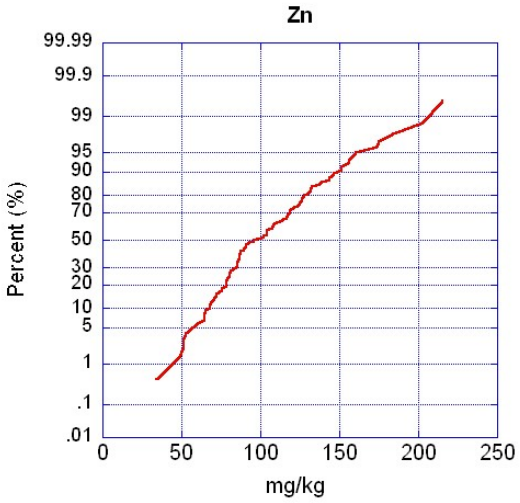
5b.30.1 Distribution of Zn concentrations

Zinc concentrations in soils of the investigated area vary from 35 mg/kg to 215 mg/kg. The distribution of its values through the Agro Aversano doesn't follow any particular trend; it can only be noticed that in the western part of the area, values are predominantly lower than 94 mg/kg, while in the eastern part they mainly range between 94 mg/kg and 156 mg/kg. High Zn values with concentrations between 165 mg/kg and 202 mg/kg occur in Cimitile, Acerra and Sant'Arpino; the highest Zn concentrations (202 mg/kg- 215 mg/kg) are found in Nola and in Macerata Campania municipalities. This random distribution of Zn contents throughout all the studied area, suggests an anthropic origin for most of the anomalously high Zn concentrations found.

In the 152/06 Environmental Law, zinc concentration limits have been fixed at 150 mg/kg in residential areas, and at 1500 mg/kg in industrial areas. As shown by the geochemical maps but also by the statistical graphs realized, the upper intervention limit is not reached in any of the sampled soils, but the lower one is exceeded in the 10% (about 11 samples) of the collected samples.


N
Zn - Zinc
(mg/kg)
202 - 215
165 - 202
129 - 165
93 - 129
57 - 93
34 - 57
191 - 210
156 - 191
126 - 156
94 - 126
77 - 94
35 - 77
No data
Capua
San Tammaro
Caserta
Marcianise
Villa di Briano
Teverola
Maddaloni
Arienzo
San Felice a Cancello
Roccarainola
Aversa
Trentola Ducenta
Caivano
Acerra
Cicciano
Parete
Tufino
Marigliano
Melito di Napoli
Visciano
Pomigliano d'Arco
Scisciano
Nola
0
5
10 Km


Zn
Count
30
25
20
15
10
5
0
0
50
100
150
200
250
mg/kg


Zn
Percent (%)
99.99
99.9
99
95
90
80
70
50
30
20
10
5
1
.1
.01
0
50
100
150
200
250
mg/kg

5c Factor scores

In the following pages the three factor score maps produced are shown. The elemental association have been identified by using a matrix containing 24 elements and applying a varimax rotation (Table 9) to minimize the number of variables with high loading on each factor. The elements with a with loading higher than 0.5 are considered as representative members of each association that results from the chosen factor model.

Table 9. *Varimax-rotated factor for 113 soil samples*

Rotated Component Matrix			
Elements	Component		
	F1	F2	F3
Ag	.068	-.152	.768
As	.396	.663	.108
Ba	.789	.495	-.021
Be	.166	.917	.075
Ca	-.070	-.701	.229
Co	.860	.167	-.123
Cu	.787	.042	.089
Ga	.437	.828	-.056
Hg	-.121	-.101	.822
K	.964	.091	.014
La	.018	.967	.030
Na	.880	.089	.008
P	.865	-.017	.323
Pb	.118	.099	.817
Rb	.919	.285	.046
Sb	-.037	-.087	.793
Sn	-.043	.161	.862
Sr	.924	.035	.119
Th	-.063	.943	-.072
Ti	.401	.825	.014
Tl	.783	.503	.044
U	.650	.551	.014
V	.917	.314	-.077
Zn	.381	-.011	.691
Total Variance %	36	25	17

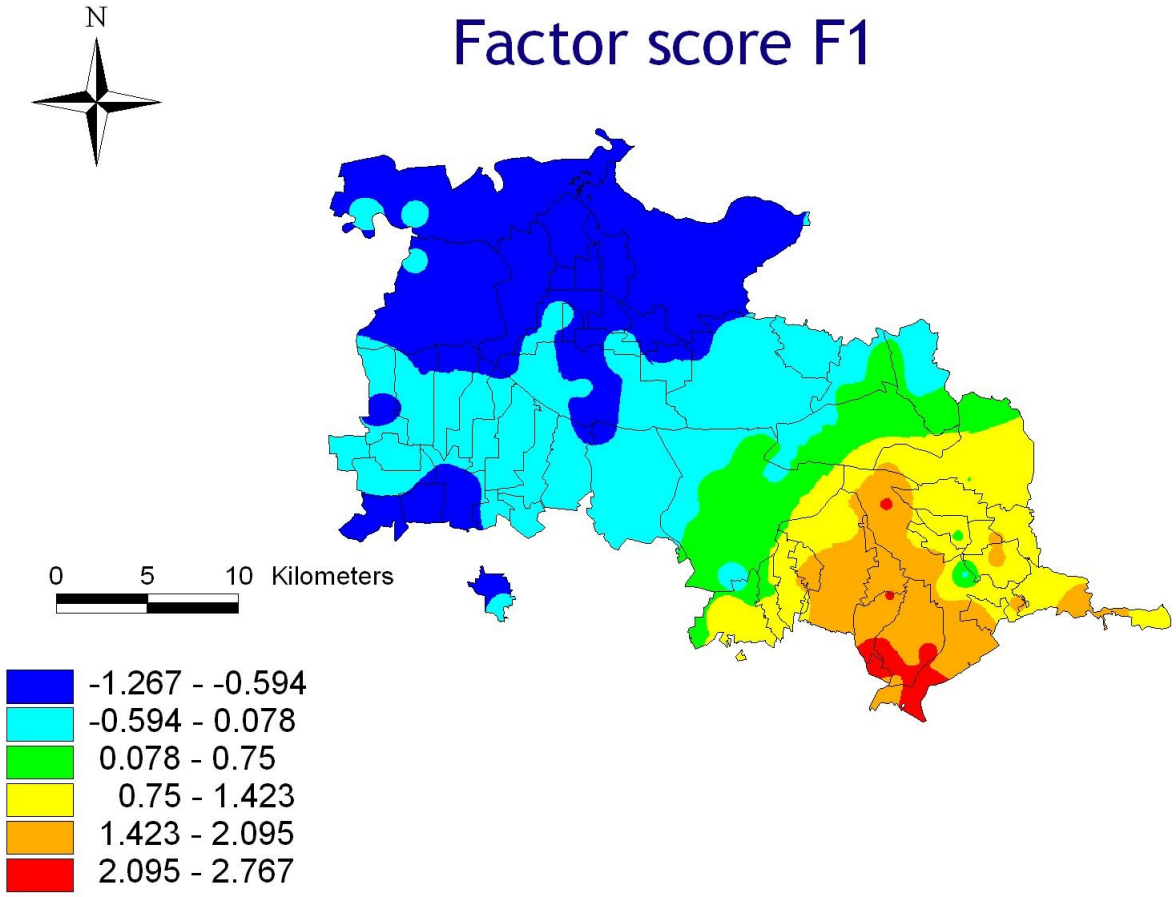
Extraction method: Principal Component Analysis Rotation method: Varimax with Kaiser normalization

5c.1 Factor score F1

The F1 factor score association accounts on the total variability of data for about 36%. It includes: K, Sr, Rb, V, Na, P, Co, Ba, Cu, Tl and U, with a loading respectively of: 0.964, 0.924, 0.919, 0.917, 0.880, 0.865, 0.860, 0.789, 0.787, 0.783, 0.650.

This factor association can be considered as the result of geogenic control on elements distribution. High and very high scores (>1.423) are all located in the south-easternmost part of the investigated area, with a peak in correspondence of southern Nola and Scisciano municipalities. Low and negative factor scores (from 0.078 to -0.594) are found in all the northern sector of the area, and their values gradually decrease when moving away from the Naples province.

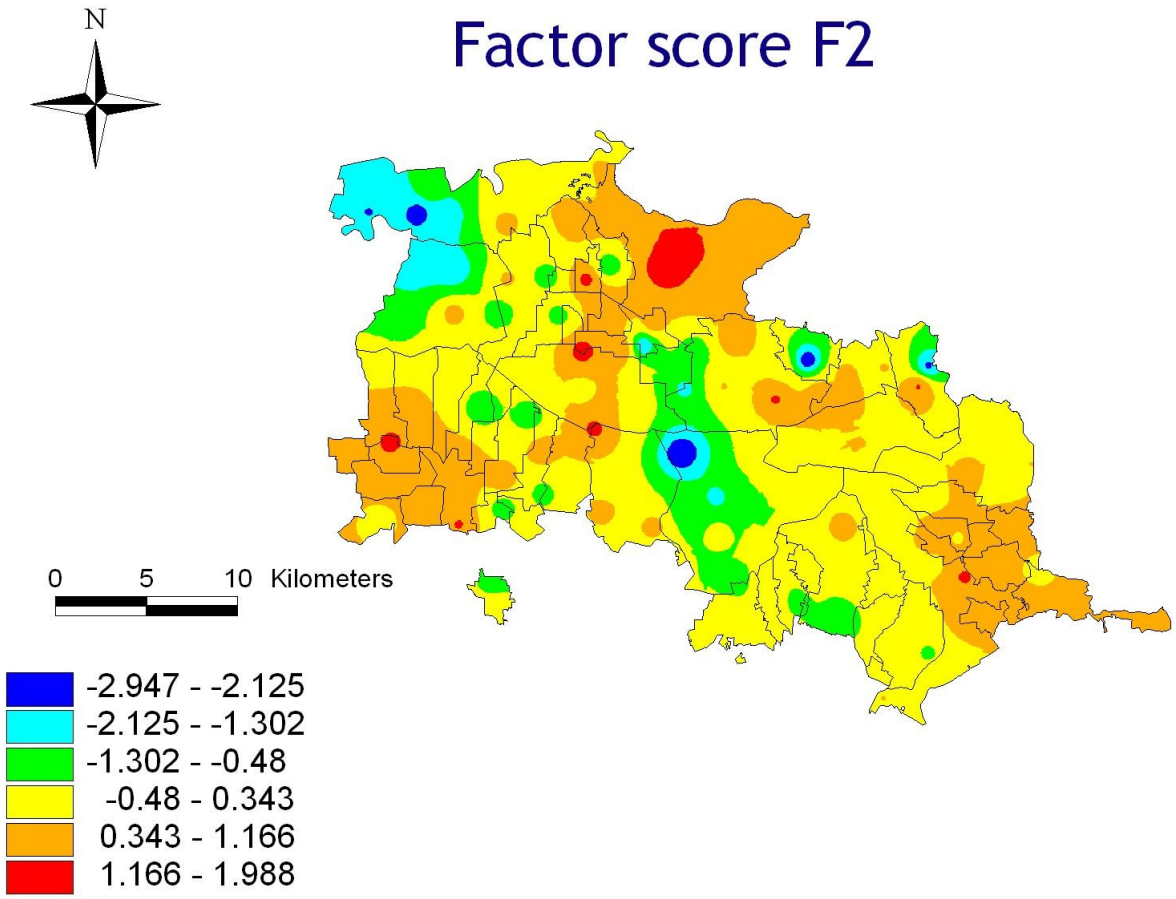
The pattern of this association suggests a strong influence of geologic origin; in the area with the highest factor scores the bedrock lithologies are the result of the volcanic activity of the Somma-Vesuvius complex and of the Campi Flegrei area, whose volcanism is potassic and ultra-potassic. The presence of metals belonging to the first and second group of the Periodic Table of Elements, such as K, Rb, Sr and Ba, with some of the highest loadings, is an evidence of the strict relationship between the factor association and the local geology.



5c.2 Factor score F2

The factor score association F2 accounts about 25% of the total data variability and is made up by La, Th, Be, Ga, Ti, As, U and Tl. The loadings of these elements are respectively: 0.967, 0.943, 0.917, 0.828, 0.825, 0.663, 0.551 and 0.503. This association is also characterized by the presence of an element with a negative loading that is calcium (-0.701).

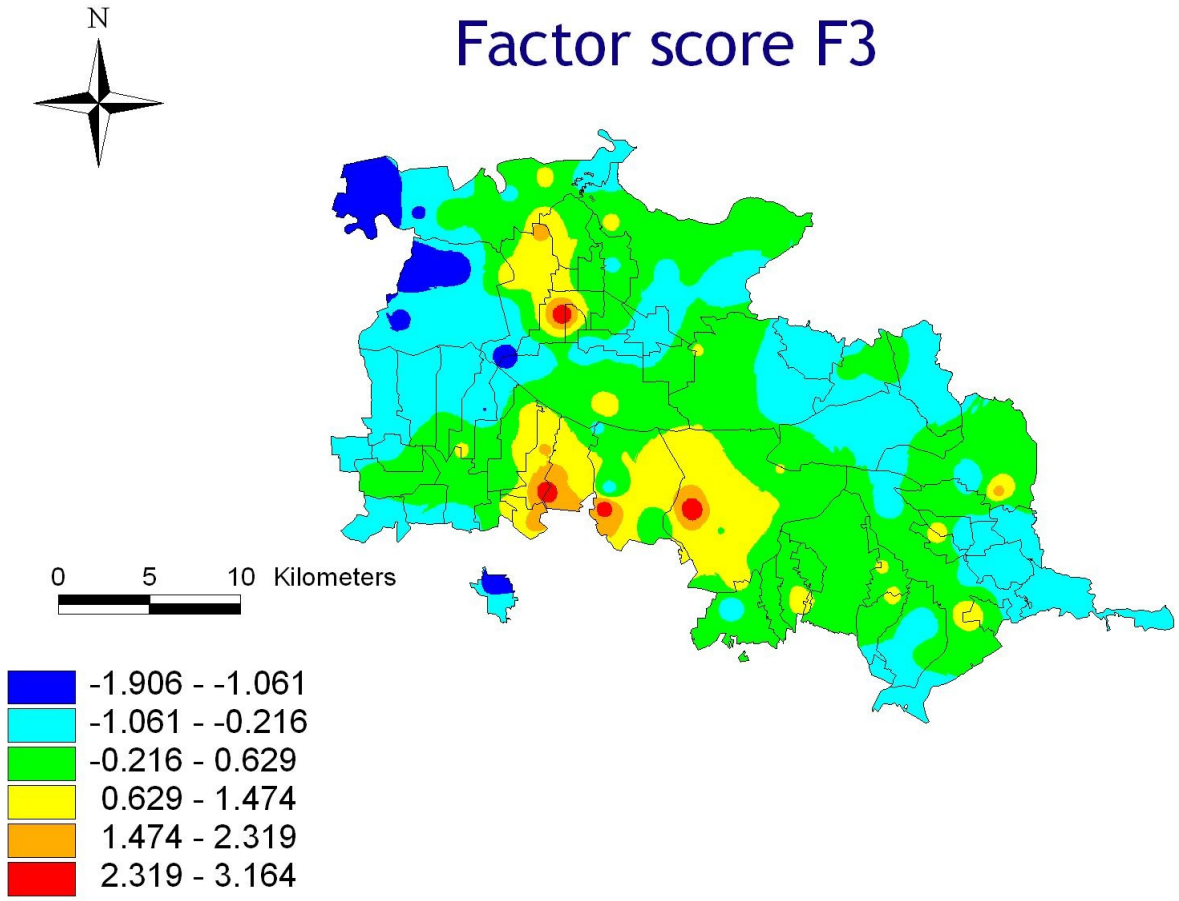
The distribution of the factor scores is not so clear as the one of the F1 association. Nevertheless is possible to identify at least two main areas in which the factors reveal a relationship with local characteristic features. In the map below, areas highlighted with the yellow color, are those with factor scores ranging between -0.48 and 0.343; highest values (1.166-1.988) are especially found in the north-eastern and in the south-western areas, that are the Caserta town and the Villa di Briano and San Marcellino municipalities. Other spots with high factor scores occur in an area between northern Caivano, Casapulla and Marcianise. The presence of such high factor scores in the area of Caserta, probably can be related to a specific local feature; it could be the result of the geochemical characteristics of the volcanic activity in northern Campania (Roccamonfina volcano). Furthermore, the negative loading of the calcium in this association, is the evidence of low amounts of carbonatic rocks where factor scores are higher.



5c.3 Factor score F3

The association of factor scores F3 accounts about 17% of the data variability and includes Sn, Hg, Pb, Sb, Ag and Zn with the following loadings: 0.862, 0.822, 0.817, 0.793, 0.768, 0.691. Most of the elements of this association are also included in the Italian Environmental Law 152/06 because considered to be particularly harmful for human health if found in excessive amounts. Data obtained by this factor score association are those related to anthropic contamination.

Most of the investigated area is characterized by factor scores below 0.629; the highest values (2.319-3.164) occur in four well identified spots: one between Macerata Campania and Portico di Caserta, and other three in the south of the Agro Aversano, respectively in Orta d'Atella, Caivano and Acerra. The distribution of these high scores doesn't follow any particular trend or local natural features and can, therefore, be related to anthropic sources of contamination.



5d Isotopic ratios

The Pb isotopic ratios obtained from TIMS analysis for surface soils (both leached and residue), soil profiles (both leached and residue), stream waters and groundwaters are all reported in Table 10.

These data have been plotted using the IGPEt software. On the X-Y axis of these graphs have been reported the $^{206}Pb/^{207}Pb$-$^{208}Pb/^{207}Pb$ ratios of our samples and those representing the isotopic signature from three of the pesticides most commonly used in the studied area: Azin Pb30, Crittam WG and Cosan's (Grezzi et al., 2010) (Tab.11). As end-members of these plots, have been chosen literature data of both geologic and anthropic sources, such as the volcanic related deposits from Vesuvius activities (Ayuso et al., 1998) (Tab.12), the gasoline (Monna et al., 1997-1999),and the aerosol deposits (Monna et al., 1999; Tommasini et al., 2000) (Tab.13).

Table 10. *Lead isotopic ratios of surface soils (Leached and Residue), soil profiles (Leached and Residue), stream waters and groundwaters.*

	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$		$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$
Surface Soils Leached				Soil Profiles Leached			
AV_6_T1	38.552	15.617	18.583	AV_P1_1	38.363	15.591	18.449
AV_11_T1	38.627	15.622	18.659	AV_P1_2	38.462	15.613	18.495
AV_18_T1	38.484	15.618	18.504	AV_P1_3	38.433	15.594	18.509
AV_23_T1	38.598	15.608	18.665	AV_P1_4	38.781	15.639	18.749
AV_38_T1	38.455	15.619	18.438	AV_P1_5	38.763	15.626	18.756
AV_46_T1	38.624	15.624	18.623	AV_P1_6	38.776	15.625	18.768
AV_59_T1	38.435	15.598	18.525	AV_P1_7	38.673	15.612	18.697
AV_65_T1	38.304	15.604	18.366	AV_P1_8	38.740	15.610	18.766
AV_67_T1	38.022	15.581	18.194	AV_P1_9	38.967	15.636	18.958
AV_79_T1	38.608	15.609	18.657	AV_P1_10	38.872	15.649	18.811
AV_87_T1	38.191	15.594	18.248	AV_P2_1	38.407	15.611	18.424
AV_117_T1	38.781	15.625	18.786	AV_P2_2	38.364	15.599	18.413
AV_121_T1	38.345	15.609	18.346	AV_P2_3	38.424	15.619	18.421
AV_123_T1	38.130	15.589	18.180	AV_P2_4	38.609	15.676	18.475
AV_128_T1	38.395	15.600	18.458	AV_P2_5	38.423	15.617	18.422
AV_141_T1	38.605	15.624	18.593	AV_P2_6	38.522	15.623	18.517
AV_152_T1	38.397	15.599	18.461	AV_P2_7	38.464	15.597	18.522
AV_153_T1	38.416	15.620	18.414	AV_P2_8	38.377	15.601	18.415
AV_162_T1	38.360	15.606	18.419	AV_P2_9	38.472	15.612	18.491
AV_166_T1	38.333	15.576	18.451	AV_P2_10	38.636	15.621	18.651
Surface Soils Residue				Soil Profiles Residue			
AV_6_T1	39.086	15.658	19.047	AV_P1_1	38.661	15.605	18.721
AV_11_T1	38.765	15.627	18.761	AV_P1_2	38.786	15.628	18.798
AV_18_T1	38.917	15.645	18.891	AV_P1_3	38.773	15.611	18.821
AV_23_T1	38.866	15.652	18.809	AV_P1_4	38.896	15.627	18.903
AV_38_T1	38.643	15.619	18.653	AV_P1_5	38.787	15.610	18.835
AV_46_T1	38.885	15.645	18.844	AV_P1_6	38.980	15.647	18.932
AV_59_T1	38.623	15.617	18.670	AV_P1_7	38.907	15.631	18.900
AV_65_T1	38.381	15.608	18.428	AV_P1_8	38.941	15.634	18.927
AV_67_T1	38.529	15.622	18.567	AV_P1_9	39.024	15.644	18.989
AV_79_T1	38.937	15.669	18.840	AV_P1_10	38.960	15.637	18.942
AV_87_T1	38.496	15.616	18.503	AV_P2_1	38.750	15.615	18.784
AV_117_T1	38.981	15.642	18.956	AV_P2_2	38.755	15.611	18.790
AV_121_T1	38.620	15.634	18.582	AV_P2_3	38.685	15.601	18.749
AV_123_T1	38.348	15.603	18.380	AV_P2_4	38.739	15.613	18.781
AV_128_T1	38.715	15.608	18.776	AV_P2_5	38.643	15.598	18.719
AV_141_T1	38.781	15.616	18.818	AV_P2_6	38.765	15.607	18.826
AV_152_T1	38.442	15.583	18.546	AV_P2_7	38.722	15.592	18.823
AV_153_T1	38.634	15.615	18.666	AV_P2_8	38.669	15.598	18.730
AV_162_T1	38.677	15.610	18.736	AV_P2_9	38.794	15.623	18.813
AV_166_T1	38.612	15.588	18.714	AV_P2_10	38.790	15.605	18.862
Stream Waters				Groundwaters			
AV_34_W1	38.453	15.592	18.560	AV_35_GW1	37.822	15.543	18.049
AV_48_W1	38.172	15.575	18.380	AV_82_GW1	37.992	15.586	18.112
AV_49_W1	38.086	15.566	18.284	AV_107_GW1	38.099	15.587	18.203
AV_65_W1	38.120	15.576	18.285	AV_136_GW1	37.942	15.568	18.071
AV_88_W1	38.313	15.619	18.360				
AV_104_W1	38.016	15.567	18.170				
AV_109_W1	38.347	15.597	18.502				
AV_110_W1	38.880	15.672	18.984				
AV_122_W1	38.101	15.577	18.257				
AV_122_W2	38.044	15.589	18.111				
AV_126_W1	37.927	15.564	18.065				

Table 11. *Main used pesticides isotopic ratios (Grezzi et al., 2010)*

Sample	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$
crittam	37.973	15.531	18.353
cosans	38.776	15.569	19.224
azin	38.775	15.616	18.711

Table 12. *Pb isotopic ratios of Vesuvius samples (Ayuso et al., 1998)*

Sample	Lithotype	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	Sample	Lithotype	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$
S1a	Pumice	39.286	15.712	19.072	R6a	Pumice	38.915	15.617	18.954
S1c	Pumice	39.154	15.673	19.042	R8	Scoria	38.991	15.643	18.948
S2(1)	Pumice	39.149	15.652	19.049	R9a	Scoria	39.049	15.661	19.004
S2(2)a	Pumice	39.130	15.669	19.061	V10	Scoria	39.252	15.709	19.120
S3(1)b	Pumice	39.067	15.658	18.966	V14	Scoria	39.011	15.633	19.024
S3(3)a	Pumice	39.098	15.667	18.975	V18	Scoria	38.984	15.627	19.018
S3(3)c	Pumice	39.018	15.644	18.950	V21	Scoria	39.070	15.664	18.987
S6(2)a	Pumice	39.168	15.693	18.990	V23	Scoria	39.093	15.667	18.987
S13(1)a	Pumice/Scoria	39.057	15.664	18.963	V34	Scoria	39.171	15.691	18.999
S20	Scoria	39.185	15.687	19.089	V35	Scoria	39.148	15.683	19.004
S21(2)f	Pumice	39.032	15.646	19.016	V42	Scoria	39.236	15.714	19.032
R1c	Scoria	39.229	15.708	19.051	V46	Scoria	39.052	15.661	18.982
R3a	Scoria	38.969	15.625	18.984	V102	Scoria	39.228	15.717	19.050
R4	Scoria	39.132	15.683	19.008					

Table 13. *Gasoline and aerosols isotopic ratios (Monna et al., 1997-1999; Tommasini et al., 2000)*

Sample	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$
Gasoline (Monna et al., 1997)					
TOTAL (F)	36.89	15.534	16.996	1.094	2.171
ESSO (F)	36.53	15.511	16.679	1.075	2.190
AGIP (F)	36.80	15.534	16.897	1.088	2.178
SHELL (F)	36.70	15.510	16.837	1.086	2.180
TOTAL (UK)	36.43	-	16.590	1.066	2.195
ESSO (UK)	36.39	-	16.540	1.068	2.191
SHELL (UK)	36.65	-	16.720	1.079	2.186
Gasoline (Monna et al. 1999)					
AGIP	-	-	-	1.066	2.205
SHELL	-	-	-	1.138	2.112
IP	-	-	-	1.085	2.166
Aerosol					
Areosol (P.EMP) (Monna et al. 1999)	-	-	-	1.149	2.110
Areosol (CT) (Monna et al. 1999)	-	-	-	1.168	2.095
Aerosol (CT) (Monna et al. 1999)	-	-	-	1.175	2.090
Aerosol (FI) (Tommasini et al. 2000)	-	-	-	1.163	2.099

5d.1 Surface soils

Surface leached samples have an isotopic composition closer to the Pb signature in aerosol, while the residues are closer to the Vesuvius rocks. Some residue samples (AV123T1 and AV65T1) have values overlapping the aerosol area, but there is a quite clear shift between the leached and the residues, the first mainly controlled by human activities and the last with a more clear dependence on the local bedrock.

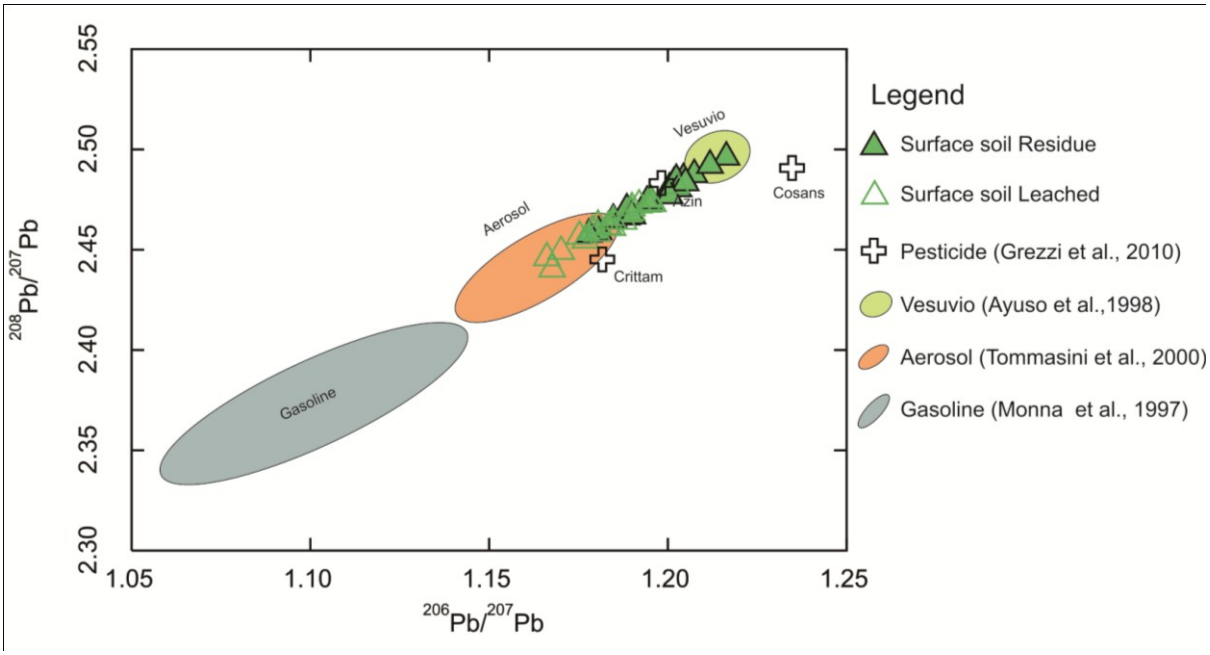


Fig.15 – *Lead isotopic ratios for surface soils*

5d.2 Profile n. 1 - Capua

In figure 16a soils collected at different depth along the profile from Capua, are plotted. Residue samples are mainly concentrated on the geogenic Pb signature while the leached have a gap between the samples AV_P1_1, AV_P1_2, AV_P1_3 and all the other samples. These are the ones collected from the surface to 30 cm depth and are, therefore, the ones more expected to be affected by urban pollution.

This evidence is also shown in figure 16b, in which, Pb isotopic ratios for each sample, have been plotted against the collection depth. Lowest 206Pb/207Pb and 208Pb/207Pb ratios occur from the surface to 30 cm depth and are those related to the anthropic contamination; ratio values have a rapid increase at 40 cm depth and then slightly increase till the bottom. In this regular trend, samples collected between 60-70 cm and between 90-100 cm depth, have values lower than the previous but always comparable to the geologic sources (1.197 and 1.202 for 206Pb/207Pb and 2.477 and 2.484 for 208Pb/207Pb).

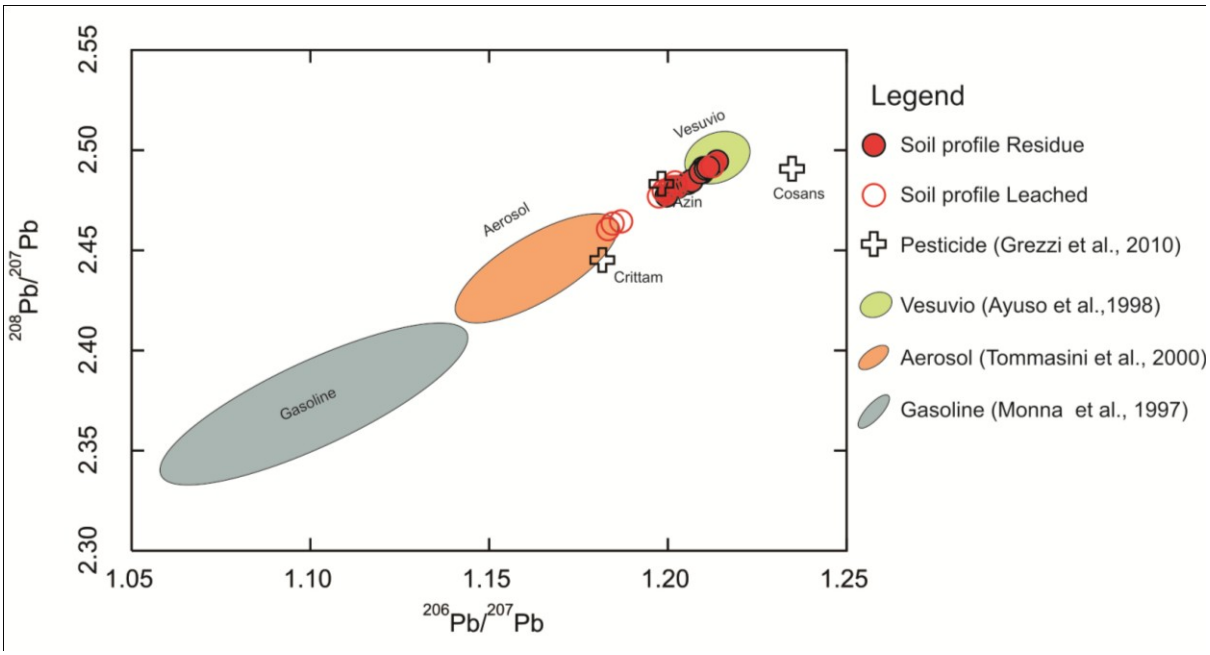


Fig.16a – *Lead isotopic ratios in soil profile n. 1 (Capua)*

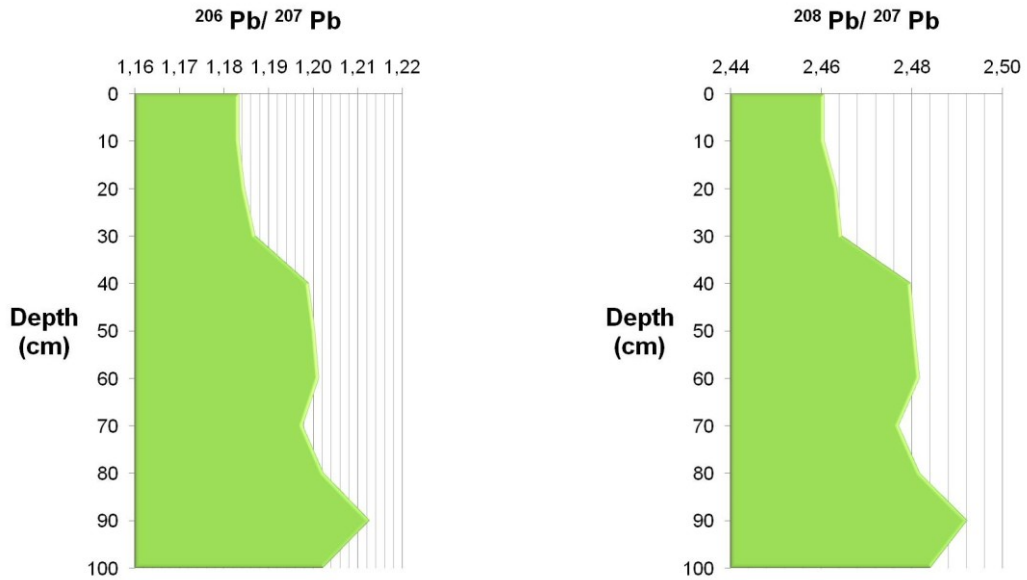


Fig.16b – *Lead ratios in soil profile n. 1(Capua). Leached samples*

5d.3 Profile n. 2 - Mariglianella

Figure 17a shows the isotopic ratios for the soil profile n. 2, collected in Mariglianella. Leached and residue Pb ratios do not overlap each other but they follow a regular trend in which residues are shifted toward the geologic signature and leached are closer to the aerosol area. The deepest leached sample and most of residues are very close to the Azin pesticide composition, while the upper leached samples have a Pb isotopic ratios closer to the Crittam pesticide.

In the next figure (Fig.17b) the variation of Pb isotopic ratios for leached soil samples collected along 1 m depth is shown. Values measured for both ratios at the top and at the bottom of the profile, are very different, showing lower values in the upper samples and lower

values at the bottom. At a depth between 30 and 80 cm Pb ratios increase and decrease without a regular trend; these significant changes are due to the Pb isotopic composition variability, and may be influenced by anthropogenic sources of contamination.

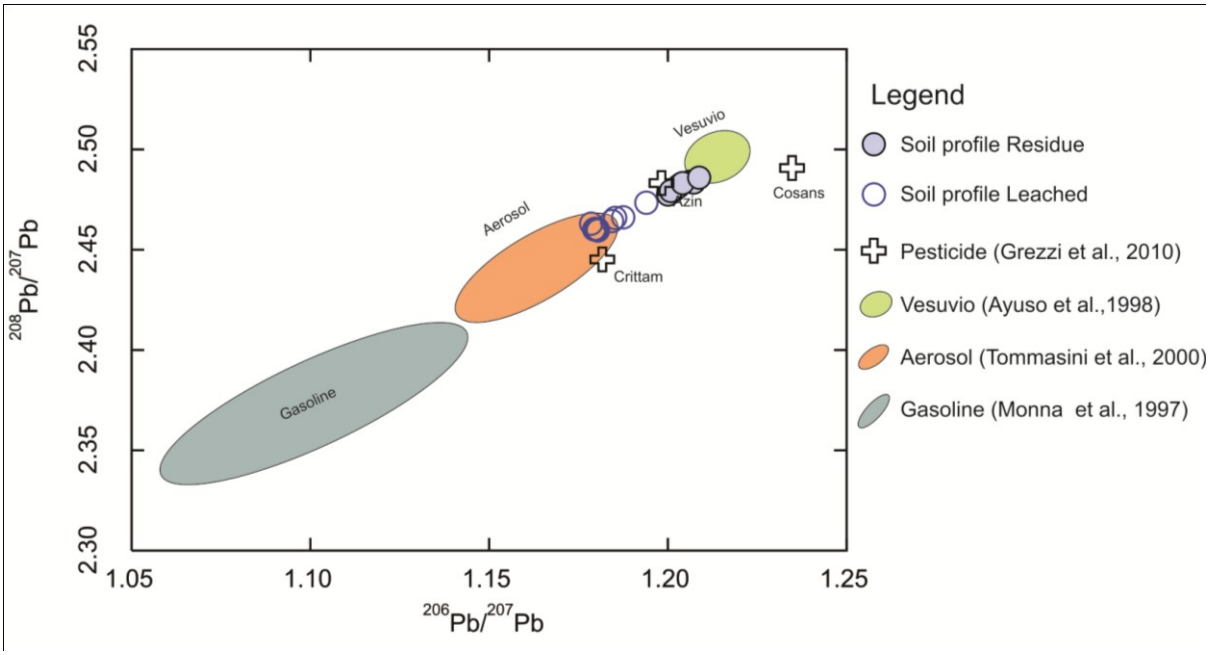


Fig.17a – *Lead isotopic ratios in soil profile n. 2 (Mariglianella)*

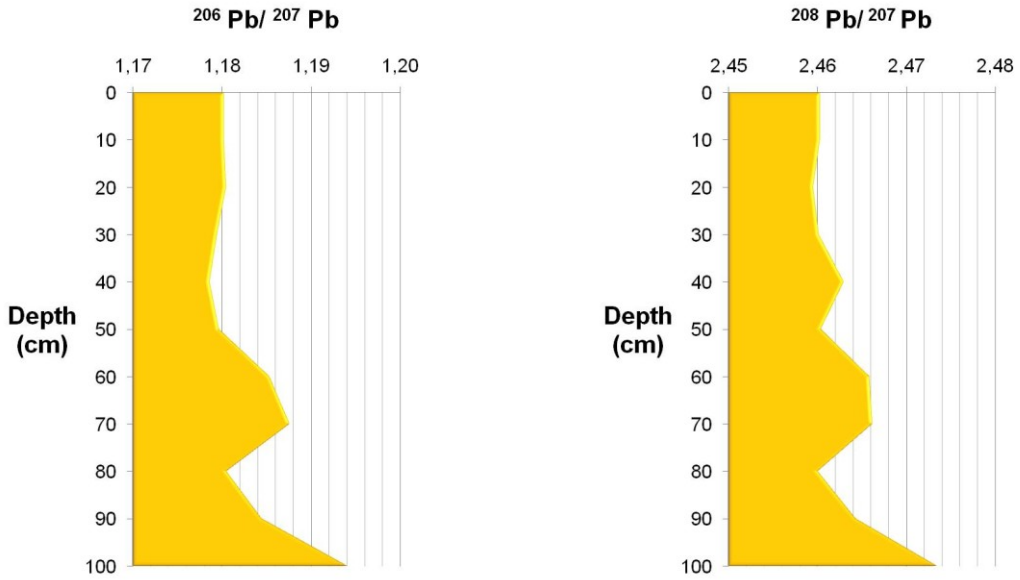


Fig.17b – *Lead ratios in soil profile n. 2 (Mariglianella). Leached samples*

5d.4 Stream waters

In figure 18 the Pb ratios measured are, for most of the stream water samples, comparable to the aerosols and Crittam pesticide values; the sample AV_110_W1, collected in Polvica, is the only one that, overlapping the Vesuvius rocks Pb signature, shows a more geogenic influence. During sampling operations almost all stream water samples had a very high turbidity level and had to be filtered before starting chemistry procedures. For this

purpose, to obtain 750 ml of filtered water from each sample, a total of 100 Millipore filters with a mesh of 0.4 μm were used. Lead ratios have been measured on filtered waters and the presence of such anthropic Pb ratio values in the samples, could be the evidence of a high interaction between water surface and aerosols, and therefore, an evidence of the high solubility of anthropogenic Pb in waters. Furthermore, the high similarity of these values with the Crittam could easily be explained by the presence of a large number of agricultural activities all along the Regi Lagni river which, during past years, have probably been using this kind of pesticide. Crittam isotopic composition could have influenced the stream running water isotopic ratios both through the run off waters and through the infiltration waters deriving from adjacent cultivated fields.

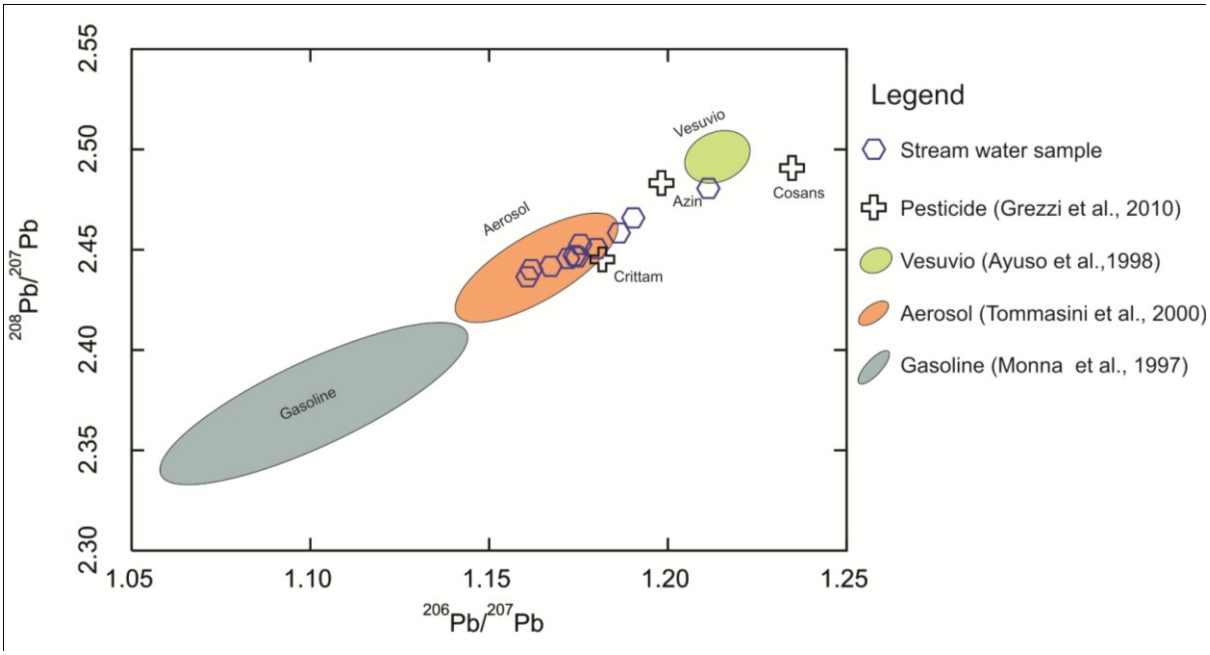


Fig.18 – *Lead isotopic ratios in stream waters*

5d.5 Groundwaters

The Pb isotopic ratios of all four groundwater samples completely fall in the area of anthropogenic gas emissions (Fig.19). In three of the four sampled sites, water is used for human consumption, in one site it's used for a cow buffaloes farm. This high correlation with the aerosol area could be related to the high rate of illegal waste disposal and sewage occurred in the Littoral Domitio-Flegreo and Agro Aversano area in the last decades. Furthermore this plot could be an evidence of the high solubility of anthropogenic Pb in soils and in the water tables and, by inference the facility with whom pollution could influence the biological cycle, affecting plants, animals and human beings.

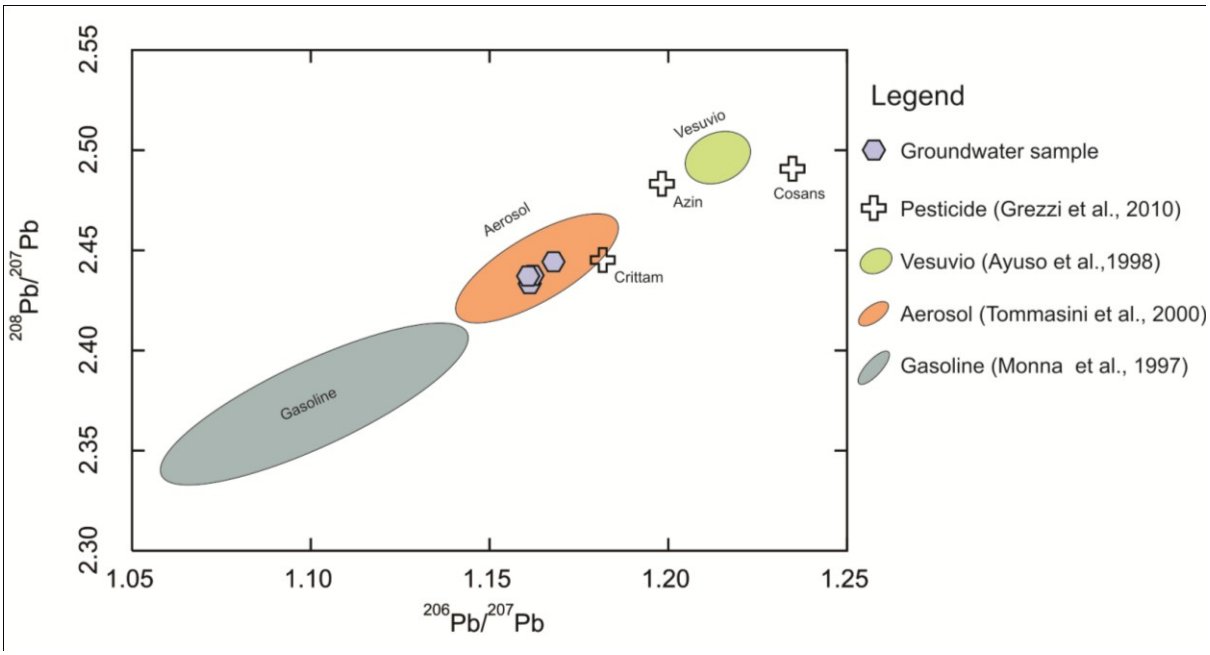


Fig.19 – *Lead isotopic ratios in groundwaters*

6 Conclusions

The results of this environmental study conducted on one of the Italian more critical areas, show how anthropic contamination is reflected on different media.

Heavy metal pollution in surface soils sampled across the Agro Aversano, exceed the intervention limits defined by the 152/06 Italian Environmental Law for residential areas only for As, Cu, Pb, Sn, Tl, V, and Zn. These values are respectively found in the municipalities of Nola, Visciano and Capua for As, in all the eastern sector of the Agro Aversano for Cu and V, in the municipalities of Marcianise, Caivano and Acerra for Pb, in all the investigated area for Sn and in most of the area for Tl. Law limits for areas with industrial destination are reached and exceeded only for Cu, in two different points at the north and at the south of Nola. The distribution of all the inorganic elements in the soils of all the investigated Domitio-Flegreo Littoral and Agro Aversano S.I.N. are reported in Lima et al. (in preparation). The Environmental Law 152/06 defines the intervention limits for heavy metals concentrations only in groundwaters and there is no specification about surface waters.

About the Pb isotopic composition of surface soils and soil profiles there is a quite clear distinction between values measured in leached samples and values measured in residue samples. For surface soils and for both soil profiles analyzed, the residue portion of samples shows a high correlation with the local isotopic imprinting of the bedrock (Ayuso et al., 1998; Tarzia et al. 2002), mainly characterized by ignimbrites, pyroclastites and other volcanics from the Vesuvius and other adjacent volcanic complexes, such as the Roccamonfina volcano and the Campi Flegrei. On the other hand, soil leached samples have Pb isotopic ratios closer to the values of the anthropic contamination measured in aerosol depositions (Monna et al., 1999; Tommasini et al. 2000). These pronounced similarities between leached samples and anthropic contamination, and between residues and geogenic sources, are what we expected from the leaching process. Before being analyzed, soil samples have been leached with 3 ml of 1.5N HCl+3N HNO3 in order to dissolve amorphous Fe- and Mn-oxyhydroxides, whose coatings are thought to catch most of the anthropogenic Pb, thus separating what could be considered secondary-deposition Pb (anthropogenic) from what could be considered first-deposition Pb (geogenic). An evidence of the connection between anthropic contamination and Pb isotopic ratios distribution could also be the variation of the ratios in soil samples collected at increasing depth (soil profiles). In both soil profiles 206Pb/207Pb and 208Pb/207Pb ratios have a significant variation from the top to the bottom; values are lower (anthropic end-member) in the more superficial samples, and increase (bedrock end-member) with the depth. This trend is not regular for all samples but can be considered increasing along the profiles with a substantial difference between the top and the bottom.

Lead ratios in filtered groundwaters and stream waters show a more clear influence of the anthropic Pb than the soils. Most of the stream waters and all of the groundwaters overlap the aerosol area; in both cases the isotopic signature is close to the Crittam pesticide, whose large use may have influenced the water isotopic composition.

Another evidence shown by the isotopic graphs is the overlap that occurs for all the soils (surface and profiles) and one particular kind of pesticide, the Azin. Its influence is very clear especially in the profile sampled in Capua. On waters also the Crittam pesticide seems to have clear influences, and this could be an evidence of the high migration of this kind of

pesticide from soils to waters. The Cosan's is the only pesticide that doesn't seem to affect soils and waters.

In conclusion it can be said that all the sampled media have been influenced in different ways by the human derived pollution and that these evidences could be the basis for further isotopic studies carried out in detailed critic areas. A more detailed isotopic study on Agro Aversano waters could be planned increasing the number of samples collected and maybe paying attention on the >0.4 μm sediments suspended in waters before their filtration.

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